

# EXHIBIT A



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**United States Patent** [19][11] **Patent Number:** **5,252,652****Egashira et al.**[45] **Date of Patent:** **Oct. 12, 1993**[54] **SOLID GOLF BALL**

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A63B 37/00

[52] **U.S. Cl.** ..... 524/392; 524/289;  
524/382; 524/908; 273/218

[58] **Field of Search** ..... 524/908, 289, 382, 392[56] **References Cited****U.S. PATENT DOCUMENTS**

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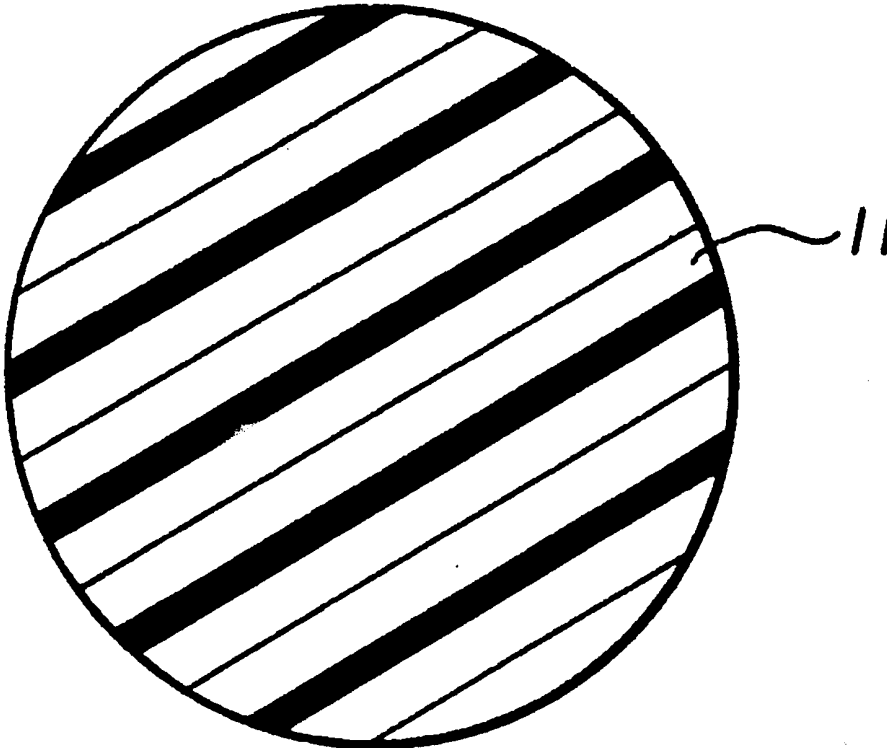
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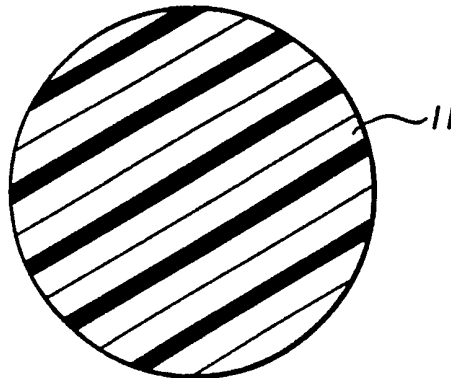
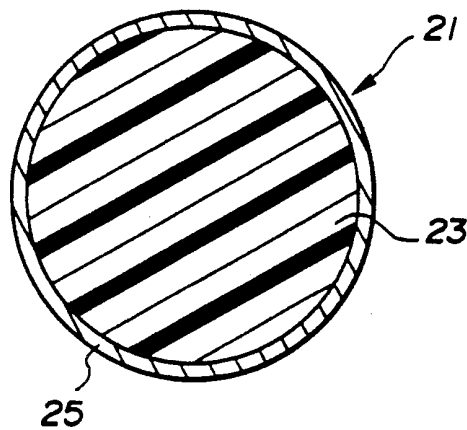
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[57]

**ABSTRACT**

One-piece and multi-layered golf balls are improved in flying performance by forming the one-piece ball entirely or multi-layered golf ball core from a rubber composition comprising a base rubber, an unsaturated carboxylic acid metal salt, and an organic sulfur compound and/or a metal salt thereof.

**13 Claims, 1 Drawing Sheet**

**FIG. 1****FIG. 2**

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**SOLID GOLF BALL**

This invention relates to solid golf balls having improved flying performance.

**BACKGROUND OF THE INVENTION**

In general, solid golf balls include a one-piece golf ball which is integrally molded in its entirety a two-piece golf ball having a core enclosed in a cover, and a multi-layered golf ball having a core enclosed in a cover through one or more intermediate layers.

These solid golf balls have an elastic portion in the form of a molded and vulcanized rubber compound as a portion, that is, a core in the case of multi-layered golf balls or as their entirety in the case of one-piece golf balls. For the purpose of improving the repulsion coefficient and impact resistance of the prior art rubber compositions from which the elastic portion was formed, attempts were made to blend a monomer having an unsaturated bond, typically an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid metal salt as a co-crosslinking agent in polybutadiene or a similar base rubber. The co-crosslinking agent will graft or crosslink to the backbone of polybutadiene rubber under the action of a peroxide or similar co crosslinking initiator, resulting in a three-dimensional crosslinked polymer, which can provide an adequate degree of hardness and durability for one-piece golf balls or multi-layered golf ball cores. Therefore, one-piece golf balls formed from rubber compositions having such a co-crosslinking agent blended and multi-layered golf balls having cores formed from rubber compositions having such a co-crosslinking agent blended are known to exhibit satisfactory flying performance and durability.

Golf players have a continuous demand for better flying performance and it is thus desired to develop golf balls having further improved flying performance.

**SUMMARY OF THE INVENTION**

Therefore, an object of the invention is to provide a golf ball having further improved flying performance.

Searching for an optimum additive for a rubber composition containing a base rubber, typically polybutadiene and an unsaturated carboxylic acid metal salt as a co-crosslinking agent, the inventors have found that when an organic sulfur compound and/or a metal-containing organic sulfur compound is added to the rubber composition, there is obtained a rubber composition which can be vulcanized into a rubbery elastomer having improved rebound resilience. If a one piece golf ball or a multi-layered golf ball core is formed from this rubber composition, the resulting solid golf ball exhibits an increased initial velocity upon hitting and improved flying performance. The present invention is predicated on this finding.

According to the present invention, there is provided a solid golf ball comprising a rubber composition containing a base rubber, an unsaturated carboxylic acid metal salt, and a sulfur compound selected from the group consisting of an organic sulfur compound and a metal-containing organic sulfur compound.

In one form, the ball is a one-piece golf ball which is entirely formed of the present rubber composition.

In another form, the ball is a multi-layered golf ball comprising a core and a cover enclosing the core, wherein the core is formed of the present rubber com-

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position. The core may be enclosed in the cover directly or through an intermediate layer.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a cross section of a one-piece golf ball.

FIG. 2 is a cross section of a two-piece golf ball.

**DETAILED DESCRIPTION OF THE INVENTION**

FIG. 1 shows in cross section a one-piece golf ball 11. FIG. 2 shows a two-piece golf ball 21 comprising a core 23 coated with a cover 25. A plurality of, usually 200 to 600, dimples are formed on the surface of the golf balls, although they are not shown in FIGS. 1 and 2.

The solid golf ball of the present invention is a one piece golf ball or a multi-layered golf ball in which the one-piece golf ball or the core of the multi-layered golf ball is formed from a rubber composition comprising a base rubber, an unsaturated carboxylic acid metal salt, and an organic sulfur compound and/or a metal-containing organic sulfur compound.

The base rubber used herein may be any desired rubber which is commonly used in conventional one-piece golf balls and cores of multi-layered golf balls. Polybutadiene rubbers, especially poly(1,4-butadiene) rubbers containing at least 40 mol %, preferably 80 to 100 mol % of cis-1,4 bond are preferred because of high rebound resilience, extrusion moldability, and high strength after vulcanization. If desired, the poly(1,4-butadiene) rubbers may be blended with natural rubber, polyisoprene rubber, styrene-butadiene rubber or the like. It is desired that at least 80% by weight of poly(1,4-butadiene) rubber be present in the base rubber because base rubbers containing less amounts of poly(1,4-butadiene) rubber often fail to take advantage of the rebound resilience of polybutadiene rubber.

The metal salt of unsaturated carboxylic acid is blended as a co-crosslinking agent. Examples include zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms, such as acrylic acid, methacrylic acid, maleic acid, and fumaric acid, with the zinc salts of acrylic and methacrylic acid being most preferred. The unsaturated carboxylic acid metal salt may be blended in a rubber either as a preformed metal salt or by introducing an  $\alpha,\beta$ -unsaturated carboxylic acid and a metal oxide or hydroxide into the rubber composition and allowing them to react in the rubber composition to form a metal salt. The unsaturated carboxylic acid metal salt may be blended in any desired amount, but preferably in amounts of about 25 to about 40 parts by weight per 100 parts by weight of the base rubber.

The rubber composition used in the manufacture of the solid golf ball of the invention contains an organic sulfur compound and/or a metal-containing organic sulfur compound in addition to the base rubber and the unsaturated carboxylic acid metal salt. Examples of the organic sulfur compound include thiophenols such as pentachlorothiophenol, 4-butyl-o-thiocresol, 4 t-butyl-p-thiocresol, and 2-benzamidothiophenol, thiocarboxylic acids such as thio-benzoic acid, and sulfides such as dixylyl disulfide, di(o-benzamidophenyl) disulfide and alkylated phenol sulfides. Examples of the metal-containing organic sulfur compound include zinc salts of the above-mentioned thiophenols and thiocarboxylic acids. The sulfur compounds may be used alone or in admixture of two or more of them. The sulfur compound is preferably blended in amounts of from about 0.05 to about 2 parts by weight, more preferably from

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about 0.1 to about 0.5 parts by weight per 100 parts by weight of the base rubber.

The rubber composition of the invention may further contain a co-crosslinking initiator. Preferred examples of the co-crosslinking initiator include organic peroxides, such as dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl-cyclohexane, n-butyl-4,4-bis(t-butylperoxy)valerate, 2,2-bis(t-butylperoxy-isopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene, with the dicumyl peroxide being most preferred. The initiator may be blended in amounts of about 0.5 to about 3 parts by weight, preferably about 1 to about 2.5 parts by weight per 100 parts by weight of the base rubber.

Also employable is a filler. Preferred examples of the filler include metal oxides such as zinc oxide and magnesium oxide. It may be blended in amounts of about 10 to about 80 parts by weight per 100 parts by weight of the base rubber. If desired, the rubber composition can additionally contain a plasticizer, an antioxidant, and any other additives which are generally employed in the preparation of one-piece balls or cores of multi-layered balls. Their amounts may be determined without undue experimentation.

The solid golf ball of the invention may be prepared by molding the above-formulated rubber composition as formulated above into a desired spherical shape, that is, a ball in the case of a one-piece ball or into a core in the case of a multi-layered ball and vulcanizing the rubber by heating. The manufacture may be in accord with conventional method and conditions.

When multi-layered golf balls such as two-piece balls are manufactured, the core is coated with a cover. The cover material used herein may be selected from commonly used cover materials, for example, ionomers such as Surlyn®, polyesters, and nylons. The cover usually has a thickness of 0.5 to 2.5 mm.

The core may be enclosed in the cover directly or through an intermediate layer.

The present invention may be applied to any type of golf ball including small balls having a diameter of at least 41.15 mm and a weight of up to 45.92 g, and large balls having a diameter of at least 42.67 mm and a weight of up to 45.92 g.

The distribution and total number of dimples are not critical although 300 to 550 dimples, preferably 350 to 540 dimples are generally formed on a ball. Preferred dimple arrangements are regular icosahedral, regular dodecahedral, and regular octahedral arrangements. The dimples is preferably distributed uniformly on the ball surface in such an arrangement.

The solid golf balls of the invention are of the above-mentioned construction and exhibit excellent flying performance.

#### EXAMPLE

Examples of the invention are given below together with comparative examples by way of illustration and not by way of limitation.

#### EXAMPLES 1-6

Solid cores for two-piece golf balls were prepared and compared with conventional two-piece golf ball cores.

Six rubber compositions were prepared by mixing the ingredients shown in Table 1. A two-piece golf ball-forming solid core having a diameter of 38.0 mm was prepared by molding each of the compositions in a mold

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followed by vulcanization at 155° C. for 20 minutes. The cores were examined by a hitting test according to the USGA standard. Using a hitting machine of the flywheel type, the cores were hit at a head speed of 38 m/sec. to measure the initial velocity (in m/sec.). The results are shown in Table 1.

TABLE 1

	Core No.					
	1	2	3	4*	5*	6*
<u>Ingredients (pbw)</u>						
Poly(cis-1,4-butadiene)	100	90	80	100	90	80
Poly(cis-isoprene)	0	10	20	0	10	20
Zinc acrylate	32	32	32	32	32	32
Zinc oxide	21	21	21	21	21	21
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2
Dicumyl peroxide	1.5	1.5	1.5	1.5	1.5	1.5
Pentachlorothiophenol zinc salt	0.2	0.2	0.2	0	0	0
Initial velocity, m/sec.	73.32	73.11	72.80	72.95	72.67	72.30

\*outside the scope of the invention

As seen from Table 1, the performance, that is, initial velocity upon hitting of the core is improved by blending zinc salt of pentachlorothiophenol which is a metal salt of an organic sulfur compound in a rubber composition.

#### Examples 7 and 8

Two rubber compositions were prepared by blending the ingredients shown in Table 2. Two-piece golf ball solid cores having a diameter of 38 mm were prepared by molding the composition in a mold and vulcanizing at 155° C. for 20 minutes. An ionomer resin composition was applied to the cores to form a cover thereon. There were obtained two-piece golf balls having a diameter of 42.7 mm.

The balls were measured for weight, hardness and initial velocity. The hardness of the balls was measured as a deflection (in mm) under a load of 100 kg. The initial velocity (in m/sec.) of the balls was measured by a hitting test according to the USGA standard in which the balls were hit at a head speed of 38 m/sec. using a hitting machine of the flywheel type. The results are shown in Table 2.

TABLE 2

	Example	
	7	8*
<u>Core composition (pbw)</u>		
Poly(cis-1,4-butadiene) rubber	100	100
Zinc acrylate	32	32
Zinc oxide	21	21
Antioxidant	0.2	0.2
Dicumyl peroxide	1.5	1.5
Pentachlorothiophenol zinc salt	0.2	—
<u>Ball properties</u>		
Weight, g	45.3	45.3
Hardness	2.30	2.32
Initial velocity, m/sec.	73.37	72.84

\*outside the scope of the invention

As seen from Table 1, the gold balls of the invention are improved in initial velocity upon hitting and hence, in flying performance.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the

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appended claims, the invention may be practices otherwise than as specifically described.

We claim:

1. A solid golf ball, having an improved rebound property and initial velocity, comprising a rubber composition containing 100 parts by weight of a base rubber selected from the group consisting of polybutadiene rubber, natural rubber, polyisoprene rubber and styrene-butadiene rubber, about 25 to about 40 parts by weight of a zinc or magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms, about 0.05 to about 2 parts by weight of a sulfur compound selected from the group consisting of pentachlorothiophenol, 4-t-butyl-o-thiocresol, 4-t-butyl-p-thiocresol, 2-benzamidothiophenol, thiobenzoic acid, and zinc salts thereof, and about 0.5 to about 3 parts by weight of an organic peroxide.

2. The solid golf ball of claim 1, wherein said solid golf ball is a one-piece golf ball which is formed of said rubber composition.

3. The solid gold ball of claim 1, wherein said solid golf ball core and a cover enclosing the core, and said core is formed of said rubber composition.

4. The solid golf ball of claim 3, wherein said solid golf ball is a two-piece ball, and said core is directly enclosed in the cover.

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5. The solid gold ball of claim 3, wherein said solid golf ball further comprises an intermediate layer between the core and the cover.

6. The solid golf ball of claim 1, wherein said base rubber is a polybutadiene rubber.

7. The solid gold ball of claim 6, wherein said polybutadiene rubber is a poly(1,4-butadiene) rubber containing at least 40 mol % of cis-1,4 bond.

8. The solid golf ball of claim 7, wherein said poly(1,4-butadiene) rubber contains at least 80 to 100 mol % of cis-1,4 bond.

9. The solid golf ball of claim 7, wherein said base rubber comprises at least 80% by weight of said poly(1,4-butadiene) rubber.

10. The solid golf ball of claim 9, wherein said poly(1,4-butadiene) rubber is blended with a natural rubber, a polyisoprene rubber of a styrene-butadiene rubber.

11. The solid gold ball of claim 1, wherein said sulfur compound is blended in an amount of from about 0.1 to about 0.5 parts by weight.

12. The solid golf ball of claim 1, wherein said organic peroxide is selected from the group consisting of dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(t-butylperoxy)valerate, 2,2'-bis(t-butylperoxyisopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene.

13. The solid golf ball of claim 1, wherein said rubber composition further comprises a filler.

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# EXHIBIT B



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**United States Patent** [19]**Higuchi et al.**[11] **Patent Number:** **5,553,852**[45] **Date of Patent:** **Sep. 10, 1996**[54] **THREE-PIECE SOLID GOLF BALL**

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[21] Appl. No.: **271,953**[22] Filed: **Jul. 8, 1994**[30] **Foreign Application Priority Data**

Jul. 8, 1993 [JP] Japan ..... 5-193065

[51] Int. Cl.<sup>6</sup> ..... **A63B 37/06**[52] U.S. Cl. .... **473/373; 473/378**[58] Field of Search ..... 273/228, 230,  
273/218, 220, 219, 225, 229, 214, 217[56] **References Cited****U.S. PATENT DOCUMENTS**

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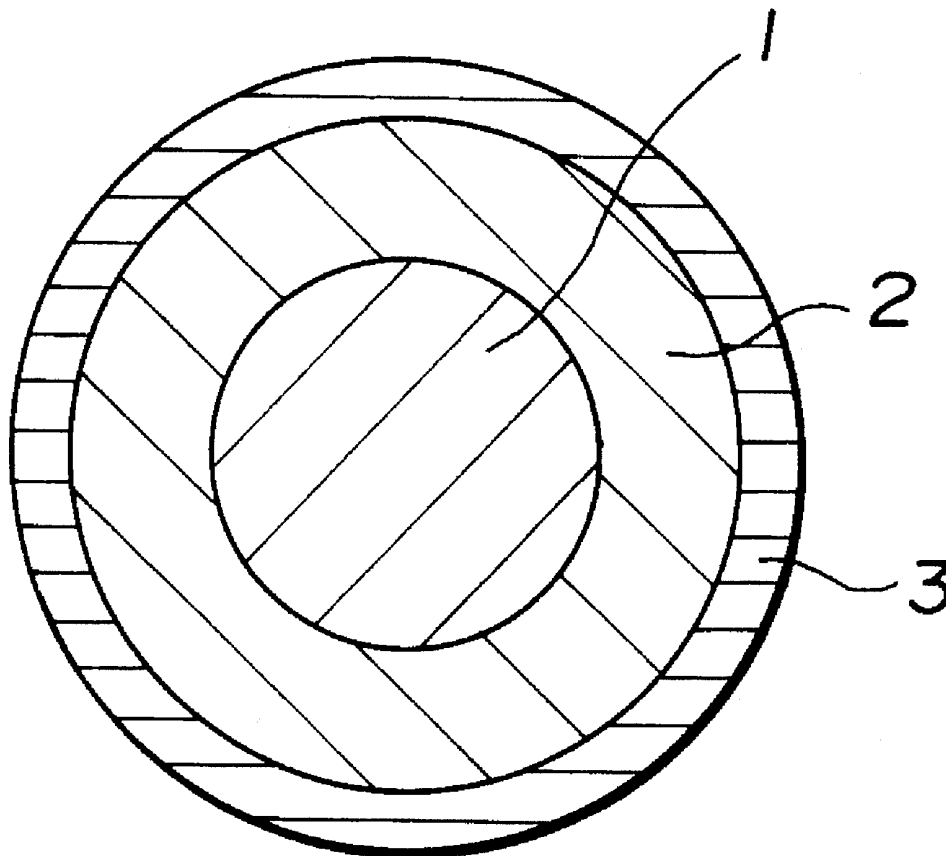
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*Primary Examiner*—George J. Marlo*Attorney, Agent, or Firm*—Sughrue, Mion, Zinn, Macpeak & Seas[57] **ABSTRACT**

A three-piece solid golf ball comprising a center core, an intermediate layer, and a cover. The center core (1) has a diameter of at least 29 mm, a hardness in the range of 45–80 JIS C and a specific gravity of less than 1.4. The intermediate layer (2) has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale. The cover (3) has a thickness of 1–3 mm and a hardness of 50–85 JIS C. The ball has a good total balance of properties in that feeling and controllability are improved at no sacrifice of flying performance and durability.

**8 Claims, 1 Drawing Sheet**

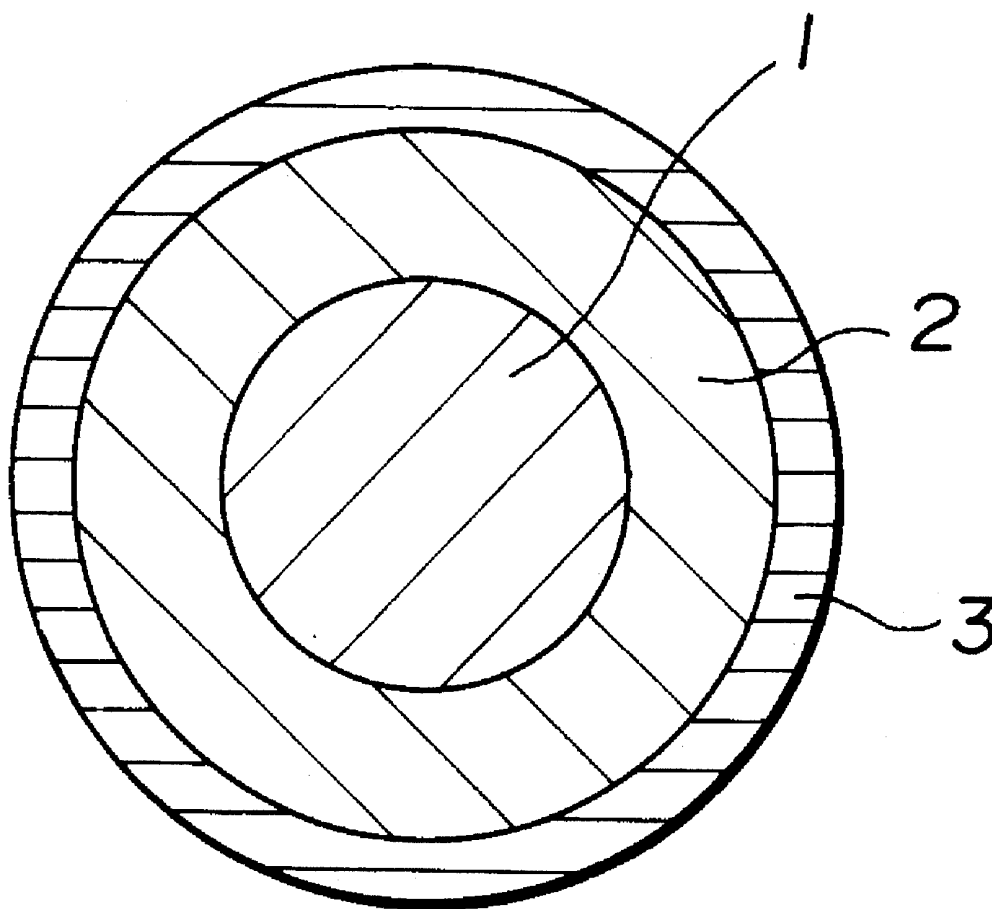


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# FIG. 1



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**THREE-PIECE SOLID GOLF BALL****BACKGROUND OF THE INVENTION****1. Field of the Invention**

This invention relates to three-piece solid golf balls comprising a center core, an intermediate layer, and a cover and more particularly, to three-piece solid golf balls which are improved in feeling on impact, controllability, and durability.

**2. Prior Art**

Among a variety of golf balls, thread-wound golf balls and solid golf balls are now popular. The solid golf balls are currently increasing to be a mainstream product. Among them, two-piece solid golf balls consisting of a core and a cover are most widespread.

Most amateur golfers are fond of two-piece solid golf balls which have excellent flying performance and durability although these balls have the disadvantages of a very hard feel on hitting and low control due to rapid ball separation on hitting. For this reason, many of professional golfers and skilled amateur golfers who impose weight on feeling and control prefer wound golf balls, especially wound golf balls using a soft balata cover, to two-piece solid golf balls. The wound golf balls are superior in feeling and control, but inferior in flying distance and durability to the two-piece solid golf balls.

Under the present situation that two-piece solid golf balls and wound golf balls have contradictory characteristics as mentioned above, players make a choice of golf balls depending on their own skill and taste.

In order to develop solid golf balls having a hitting feel approximate to the wound golf balls, two-piece solid golf balls of the soft type have been considered. For such two-piece solid golf balls of the soft type, soft cores must be used. If the cores are soft, however, repulsion becomes low with a concomitant loss of flying performance and durability is considerably deteriorated. That is, the superior flying performance and durability which are a characteristic of two-piece solid golf balls are lost, and in an extreme case, the balls become unacceptable for practical use.

Controllability, which is required even on full shots with drivers, is most important on control shots like approach shots. In an exemplary situation that the next shot should fly beyond the bunker and a short distance from the green edge to the cup, the player who is either professional or amateur will naturally wish to hit a ball with a minimal run. Such controllability of a golf ball largely depends on spin properties.

On a full shot with a club having a relatively large loft, the club loft is dominant to that the ball itself so that almost all balls are given an appropriate amount of spin and few balls overrun. However, on a approach shot over a short distance of 30 or 50 yards, balls will significantly vary in run or controllability. The major factor causing such a difference is not a basic structure, but the identity of cover material. In two-piece solid golf balls, however, covers made of soft material are effective for improving controllability, but detrimental for gaining flying distance.

**SUMMARY OF THE INVENTION**

Therefore, an object of the present invention is to provide a solid golf ball which is improved in feeling and controllability while maintaining the superior flying performance

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and durability which are characteristic of solid golf balls, that is, improved in total balance.

In connection with a solid golf ball having a core forming the center and a cover forming the outermost layer, the inventors have found that by providing a relatively hard intermediate layer between the center core and the cover, and controlling the size and specific gravity of the core, intermediate layer and cover, the center core and core can be made relatively soft to improve feeling and controllability without deteriorating flying performance and durability. The feeling and controllability can be improved in a favorable way.

Briefly stated, an intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale is formed around a center core having a diameter of at least 29 mm and a specific gravity of less than 1.4 and greater than the intermediate layer specific gravity. A cover having a thickness of 1 to 3 mm is formed on the outer surface of the intermediate layer to complete a solid golf ball. Then even when the center core is softened to a JIS C scale hardness of 45 to 80 and the cover softened to a JIS C scale hardness of 50 to 85, the feeling and controllability can be improved at no sacrifice of flying distance and durability. Further when the intermediate layer is formed of a resin composition based on a high repulsion ionomer resin, the hitting feel and controllability can be further improved with no sacrifice of flying distance and durability.

The present invention provides a three-piece solid golf ball comprising a center core, an intermediate layer, and a cover wherein the center core has a diameter of at least 29 mm and a specific gravity of less than 1.4, the intermediate layer has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale. The cover has a thickness of 1 to 3 mm. The specific gravity of the intermediate layer is lower than the specific gravity of the center core. In one preferred embodiment, the intermediate layer is formed of a composition based on a high repulsion ionomer resin.

**BRIEF DESCRIPTION OF THE DRAWING**

The sole figure, FIG. 1 is a schematic cross section of a three-piece solid golf ball according to the invention.

**DETAILED DESCRIPTION OF THE INVENTION**

Referring to FIG. 1, there is schematically illustrated a typical three-piece solid golf ball according to the invention. The ball includes a spherical center core 1 forming the center of the ball and a cover 3 forming the outermost layer of the ball. A relatively hard intermediate layer 2 is disposed between the core 1 and the cover 3. The size and specific gravity of the core 1, intermediate layer 2, and cover 3 are set in specific ranges.

The center core has a diameter of at least 29 mm, preferably 29 to 37 mm and a specific gravity of less than 1.4, preferably 1.05 to 1.38. With a diameter of less than 29 mm, the intermediate layer must be relatively thick with losses of repulsion and feeling. With a specific gravity of 1.4 or more, the ball has a heavier weight which exceeds the weight requirement of golf balls.

On an impact entailing substantial deformation as found on driver shots, the player gets a feeling which largely depend on the hardness of the center core 1 and varies with the club head speed given by the player. Therefore, the

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hardness of the center core 1 should be set in accordance with the head speed of the target players. In this sense, the center core hardness is not particularly limited although it preferably ranges from 45 to 80, more preferably from 60 to 80 on JIS C scale (at the center core surface).

The center core 1 is generally formed from a well-known rubber composition comprising a base rubber, co-crosslinking agent and peroxide through heating, pressing and molding steps. The base rubber may be one conventionally used in solid golf balls and preferably be selected from polybutadiene rubber and mixtures of polybutadiene rubber and polyisoprene rubber. Use of 1,4-polybutadiene rubber containing more than 90% of cis structure is preferred for high repulsion. The co-crosslinking agents used in conventional solid golf balls include zinc and magnesium salts of unsaturated fatty acids such as methacrylic acid and acrylic acid and esters of unsaturated fatty acids such as trimethylpropane trimethacrylate and they may be used in the present invention. Zinc acrylate is preferred for high repulsion. The co-crosslinking agent is blended in amounts of about 15 to 30 parts by weight per 100 parts by weight of the base rubber. The peroxide may be selected from a variety of peroxides, preferably dicumyl peroxide and mixtures of dicumyl peroxide and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane. The peroxide is blended in amounts of about 0.5 to 1 part by weight per 100 parts by weight of the base rubber. If desired, zinc oxide and barium sulfate may be blended in the rubber composition for specific gravity adjustment while antioxidants may also be blended.

The intermediate layer 2 has a radial thickness of at least 1 mm, preferably 1.5 to 3.5 mm, a specific gravity of less than 1.2, preferably 0.9 to 1 and lower than the center core specific gravity, and a hardness of at least 85, preferably 85 to 100 on JIS C scale. With a thickness of less than 1 mm, repulsion is lowered to reduce flying distance. With a specific gravity of 1.2 or more, the center core must have a relatively low specific gravity so that the golf ball may be increased in inertia moment and reduced in spin property and thus lose some controllability. A similar detrimental effect is observed when the intermediate layer specific gravity is greater than the center core specific gravity. A layer with a JIS C scale hardness of less than 85 detracts from flying performance. The intermediate layer preferably has an outer diameter of 38 to 41 mm though not limited thereto. Also preferably the difference in specific gravity between the center core and the intermediate layer is 0.1 or more, especially 0.1 to 0.5 though not limited thereto.

The intermediate layer 2 is effective in compensating for lowering repulsion of the center core 1 which is made soft. It is then formed of a relatively hard (JIS C scale hardness  $\geq 85$ ), repulsive material. Although the material is not critical, preferred materials are ionomer resins, for example, Himilan 1706 and 1605 commercially available from Mitsui-dupont Polychemical K.K. and Surlyn commercially available from E.I. duPont. A 1:1 blend of Himilan 1706 and Himilan 1605 is most preferred. In addition to the ionomer resin, the composition of which the intermediate layer is formed may further contain weight control agents, for example, inorganic fillers such as zinc oxide and barium sulfate, coloring agents such as titanium dioxide, and other additives.

The cover 3 has a radial thickness of 1 to 3 mm, preferably 1.5 to 2.5 mm. A cover more than 3 mm thick is low in repulsion whereas a cover less than 1 mm thick is low in durability such as cut resistance. Although the hardness of the cover 3 is not particularly limited, it is preferably set in a relatively soft range of 50 to 85, more preferably 60 to 85 on JIS C scale because in this range, improvements in all of repulsion (flying performance), durability and controllability are expected.

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The cover 3 is generally formed of resinous materials which are conventionally used as the cover of solid golf balls, preferably those materials which are relatively soft (JIS C scale hardness 50 to 85) and highly repulsive. Examples include ionomer resins such as Himilan 1650 commercially available from Mitsui-dupont Polychemical K.K., Surlyn 8120 commercially available from E.I. duPont, and mixtures thereof, thermoplastic polyester elastomers such as Hytrel 4047 commercially available from Toray-dupont K.K., and balata resins. If necessary, inorganic fillers may be blended in these resins for coloring purposes.

#### EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

#### Examples and Comparative Examples

Using a center core, intermediate layer, and cover having the composition shown in Table 1, three-piece solid golf balls (Examples 1-6, Comparative Examples 1-3) were prepared. The center core was prepared by kneading the respective components in a roll mill and pressure molding at 155° C. for 15 minutes. The intermediate layer was formed by injection molding so as to enclose the outer surface of the center core. The cover was formed around the intermediate layer by injection molding. The three-piece solid golf balls were completed in this way. The parameters associated with the core, intermediate layer and cover are shown in Table 2.

The golf balls were evaluated for spin characteristic, flying performance, feeling, and durability by the following tests. The results are shown in Table 2.

#### Spin Characteristic

Using a swing robot manufactured by True Temper Co., the ball was hit by the driver at a head speed of 45 m/s (abbreviated as W1 HS45 in Table 2) and by the sand wedge at a head speed of 17.6 m/s (abbreviated as SW HS17.6 in Table 2). The ball spin (rpm) was observed using a science eye (manufactured by Bridgestone Corporation).

#### Feeling

Professional golfers evaluated a feeling on impact according to the following criterion.

- : good
- △: average
- ×: poor

#### Flying Performance

In the spin and feeling tests, the flying distance the ball traveled was also measured. Total evaluation was made according to the following criterion.

- : good
- △: average
- ×: poor

#### Durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/s until the ball was broken. With the number of hits counted, the ball was rated according to the following criterion.

- : good
- △: average
- ×: poor

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TABLE 1

	Example						Comparative Example		
	1	2	3	4	5	6	1	2	3
<u>Center core</u>									
Cis-1,4-polybutadiene	100	100	100	100	100	100	100	100	100
Zinc acrylate	20	20	20	30	20	20	20	25	20
Zinc oxide	56	36	36	20	23	10	90	25	55
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Dicumyl peroxide	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
<u>Intermediate layer</u>									
Himilan 1706	50	50	50	50	50	50	50	50	50
Himilan 1605	50	50	50	50	50	50	50	50	50
<u>Cover</u>									
Himilan 1650	50	50	50			50	50		50
Surlyn 8120	50	50	50			50	50		50
Hytrel 4047				100				100	
Trans-isoprene rubber					90				
Natural rubber					10				

Note:

The amounts of components blended are parts by weight and their proportion is independent among the center core, intermediate layer, and cover.

TABLE 2

	Example						Comparative Example		
	1	2	3	4	5	6	1	2	3
<u>Center core</u>									
Outer diameter, mm	31.52	35.28	35.28	35.28	35.29	36.40	27.68	35.24	31.52
Hardness, JIS C	66	66	66	79	66	66	66	73	66
Specific gravity	1.36	1.24	1.24	1.19	1.16	1.07	1.56	1.19	1.35
<u>Intermediate layer</u>									
Thickness, mm	3.4	1.7	2.2	2.2	1.7	2.0	5.7	1.8	1.6
Hardness, JIS C	91	91	91	91	91	91	91	82	91
Specific gravity	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.97	0.95
Outer diameter, mm	38.35	38.73	39.65	39.66	38.73	40.40	39.00	38.91	34.56
<u>Cover</u>									
Thickness, mm	2.2	2.0	1.5	1.5	2.0	1.8	1.8	1.9	4.0
Specific gravity	0.97	0.97	0.97	1.10	1.13	0.97	0.97	1.10	0.97
Hardness, JIS C	82	82	82	61	78	82	82	61	82
<u>Ball</u>									
Outer diameter, mm	42.68	42.67	42.67	42.70	42.70	44.00	42.65	42.63	42.65
Weight, g	45.50	45.45	45.50	45.55	45.53	45.60	45.50	45.55	45.50
<u>Performance</u>									
Spin (rpm) W1 HS45	3300	3020	3030	3920	3600	3030	35	3600	3250
SW HS17.6	3900	4000	4300	6390	5800	4100	4100	4050	3500
Feeling	Δ	○	○	Δ	○	○	X	○	○
Flying performance	○	○	○	○	Δ	○	X	X	X
Durability	○	○	○	○	○	○	○	○	○

As is evident from Table 2, the three-piece solid golf balls of the present invention have a good balance of properties in that the center core and cover can be made soft to ensure a pleasant feeling and controllability (spin) without deteriorating flying performance and durability.

There has been described a three-piece solid golf ball which includes a core, intermediate layer and cover having controlled size, hardness and specific gravity so that the ball has a good total balance of properties in that a relatively soft center core and cover are used to ensure a pleasant feeling and controllability at no sacrifice of flying performance and durability.

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Japanese Patent Application No. 5-193065 is incorporated herein by reference.

Although one preferred embodiment have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A three-piece solid golf ball comprising; a center core, an intermediate layer, and a cover enclosing the core through the intermediate layer,

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said center core having a diameter of at least 29 mm and a specific gravity of less than 1.4,

said intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale, the specific gravity of said intermediate layer being lower than the specific gravity of said center core, and

said cover having a thickness of 1 to 3 mm and being softer than said intermediate layer.

2. The golf ball of claim 1 wherein said intermediate layer is formed of a high repulsion ionomer resin base composition.

3. The golf ball of claim 1 wherein said center core has a hardness of 45 to 80 on JIS C scale and said cover has a hardness of 50 to 85 on JIS C scale.

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4. The golf ball of claim 1 wherein said center core is comprised of a polybutadiene base rubber composition.

5. The golf ball of claim 1 wherein the diameter of said center core is in the range of 29–37 mm.

6. The golf ball of claim 1 wherein a difference in the specific gravity between the center core and the intermediate layer is in the range of 0.1 to 0.5.

7. The golf ball of claim 1 wherein the specific gravity of said intermediate layer is in the range of 0.9 to 1.0.

8. The golf ball of claim 1 wherein the hardness of said intermediate layer is in the range of 85–100 on JIS C.

\* \* \* \* \*

# EXHIBIT C



US005743817A

**United States Patent** [19]**Yamagishi et al.**[11] **Patent Number:** **5,743,817**[45] **Date of Patent:** **Apr. 28, 1998**[54] **GOLF BALL**[75] Inventors: **Hisashi Yamagishi; Yoshinori Egashira; Hideo Watanabe**, all of Chichibu, Japan

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**FOREIGN PATENT DOCUMENTS**[73] Assignee: **Bridgestone Sports Co., Ltd.**, Tokyo, Japan

2276628 10/1994 United Kingdom .

[21] Appl. No.: **536,049***Primary Examiner*—George J. Marlo[22] Filed: **Sep. 29, 1995***Attorney, Agent, or Firm*—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC[30] **Foreign Application Priority Data**

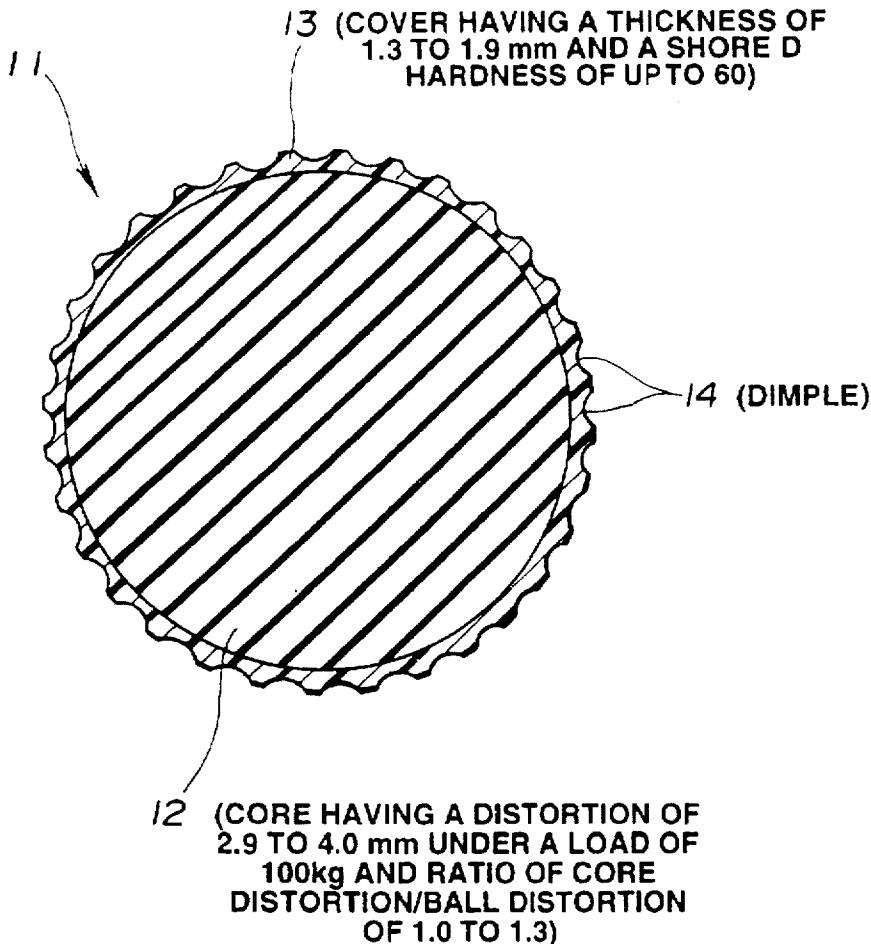
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[57] **ABSTRACT**[51] **Int. Cl.<sup>6</sup>** ..... **A63B 37/06; A63B 37/12**[52] **U.S. Cl.** ..... **473/377; 473/351; 473/385**[58] **Field of Search** ..... 473/372, 373, 473/351, 377, 385, 370, 374, DIG. 22

A solid golf ball comprising a core and a cover is provided. The core has a core hardness expressed by a distortion of 2.2–4.0 mm under a load of 100 kg. The core hardness divided by the ball hardness ranges from 1.0 to 1.3. The cover has a thickness of 1.3–1.8 mm. The ball is improved in feel and spin while maintaining the flying distance inherent to solid golf balls.

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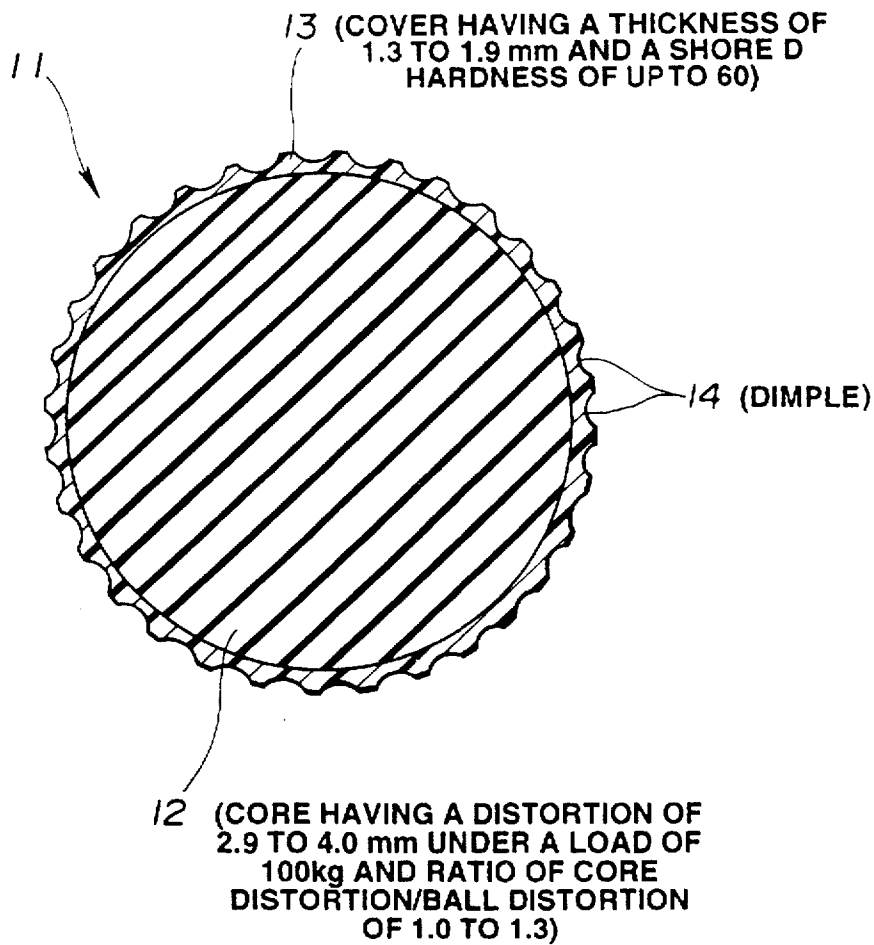
**2 Claims, 1 Drawing Sheet**

U.S. Patent

Apr. 28, 1998

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FIG. 1





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**GOLF BALL****BACKGROUND OF THE INVENTION****1. Field of the Invention**

This invention relates to a solid golf ball having improved feel and spin performance.

**2. Prior Art**

As compared with wound golf balls, two-piece golf balls and other solid golf balls are advantageous in gaining a flying distance since they fly along the trajectory of a straight ball when hit by both drivers and irons. This advantage is mainly attributable to their structure. Because of their configuration less receptive to spin, the solid golf balls are given a straight ball trajectory and yield a more run, resulting in an increased total flying distance.

In turn, the solid golf ball tends to draw a "flier" path on an iron shot since it is less receptive to spin and does not readily stop on the green. Because of such characteristics, the two-piece balls are not preferred by experienced players.

Therefore, there is a need for a solid golf ball having improved spin properties and allowing the player to aim the pin dead with an iron. The increased flying distance inherent to the solid golf ball should be maintained and of course, the ball should have a pleasant feel.

**SUMMARY OF THE INVENTION**

Therefore, an object of the present invention is to provide a solid golf ball such as a two-piece golf ball which is improved in feel, spin properties and iron control without detracting from the trajectory and flying distance inherent to the solid golf ball. The term iron control is the controllability of a ball on an iron shot, more specifically stop on the green.

Briefly stated, the present invention pertains to a solid, typically two-piece, golf ball comprising a core and a cover enclosing the core. The hardness of the core, cover and ball are referred to as core hardness, cover hardness, and ball hardness, respectively. According to the invention, the core hardness is such that the core undergoes a distortion of at least 2.2 mm under a load of 100 kg. The core hardness divided by the ball hardness is in the range of 1.0 to 1.3. The cover has a radial thickness of 1.3 to 1.8 mm. This parameter control leads to a golf ball satisfying the requirements of flying distance, feel and spin.

Consider the spin mechanism of golf balls made of the same materials, but changed in hardness. Provided that the club head speed and the cover material are identical, the coefficient of friction between the ball and the club face is identical and hence, an identical frictional force is exerted therebetween. Only distortion is different due to differential hardness. Then the distance between the center of gravity and the ball-club contact point is different. The harder the ball, the longer is the contact point distance. The softer the ball, the shorter is the contact point distance. Then harder balls are more receptive to spin.

The spinning mechanism associated with an iron suggests that the spin quantity can be increased by increasing the ball hardness. Increasing the ball hardness, however, gives a harder feel, exacerbating the hitting feel. The spin quantity can also be increased by making the cover softer. A softer cover, however, deprives the ball of repulsion, resulting in a loss of initial speed and flying distance.

Attempting to increase the spin quantity for improving spin properties by using a soft material, typically a material having a Shore D hardness of 60 or lower as the cover, we found that a low hardness cover lowers repulsion, resulting

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in a loss of flying distance on hitting. Quite unexpectedly, we have found that by adjusting the core hardness to a distortion of at least 2.2 mm under a load of 100 kg, the ratio of core hardness to ball hardness to range from 1.0 to 1.3 and the cover thickness to range from 1.3 mm to 1.8 mm, the golf ball, whose cover is made of a softer material, is improved in iron control (that is, stop on the green) without deterring the feel and flying distance and without losing the trajectory and flying distance on a driver shot inherent to solid golf balls.

**BRIEF DESCRIPTION OF THE DRAWING**

FIG. 1 is a schematic cross section illustrating one embodiment of the golf ball of the present invention.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In the golf ball comprising a spherical solid core enclosed in a cover according to the present invention, the core hardness is at least 2.2 mm as expressed by a distortion under a load of 100 kg, the core hardness divided by the ball hardness is in the range of 1.0 to 1.3 and the cover has a thickness of 1.3 to 1.8 mm.

The core hardness and ball hardness are defined by distortions (in mm) of the core and ball under a load of 100 kg, respectively. The core hardness corresponds to such a distortion of at least 2.2 mm, preferably at least 2.5 mm, more preferably 2.5 to 4.0 mm, most preferably 3.0 to 4.0 mm. With a core distortion of less than 2.2 mm, the feel becomes unpleasant. Too much core distortions would result in balls having poor restitution, low flying performance and a too soft feel. By controlling the core hardness/ball hardness so as to fall in the range between 1.0 and 1.3, especially between 1.0 and 1.25, the solid golf ball, typically two-piece golf ball is improved in feel, flying distance and spin characteristics. If the core hardness/ball hardness is less than 1.0, the feel becomes unpleasant. If the core hardness/ball hardness exceeds 1.3, the ball loses a quick stop on the green.

It is understood that the golf ball of the invention is advantageously applied to two-piece golf balls having a single core. It is also applicable to multi-core golf balls having a core consisting of two or more layers, such as three-piece golf balls. In an example where the core consists of two inner and outer layers, the core hardness refers to the hardness of the spherical two-layer core as a whole. Differently stated, the core hardness refers to the hardness of an entire spherical core left after removing the cover from the ball.

The cover has a Shore D hardness of up to 60, especially 55 to 60. A cover hardness of more than 60 would adversely affect spin characteristics and stop on the green. Since a cover with too low hardness would result in poor repulsion and a loss of flying distance, the lower limit of 55 is recommended for the cover hardness.

According to the invention, the cover has a radial thickness of 1.3 to 1.8 mm, especially 1.4 to 1.8 mm. Outside the range, the objects of the invention cannot be achieved. A cover of thinner than 1.3 mm is less resistant against top damage and liable to be broken. A cover of thicker than 1.8 mm leads to losses of repulsion and flying performance and gives a dull feel.

In general, the flying distance the ball covers depends on the head speed. The flying distance is reduced by a change from a higher head speed to a lower head speed. The degree

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of reduction of the flying distance by a change from a higher head speed to a lower head speed can be suppressed by limiting the cover thickness to the above-defined range. Differently stated, the dependency of flying distance on head speed is alleviated. Therefore, the ball of the invention is suitable for senior and female players who swing at a relatively low head speed.

In one preferred embodiment of the invention, the golf ball has a spin factor of 1.0 to 1.5. The spin factor is defined as follows. The golf ball has a spin quantity when hit by a pitching wedge (referred to as wedge spin quantity) and a spin quantity when hit by a driver (referred to as driver spin quantity). The spin factor is obtained by dividing the ratio of the wedge spin quantity to the driver spin quantity by the ball hardness. Then a spin factor smaller than unity means that the ball has greater spin with the driver and less spin with the pitching wedge. The former indicates that the trajectory is lofted and the flying distance is reduced. The latter indicates that when hit with an iron, the ball draws a flier-like trajectory and flies too much. A greater spin factor is then desirable. Then the object of the invention to render the ball receptive to less spin with a driver and more spin with an iron is effectively accomplished. However, a too greater spin factor would exacerbate ball control on an iron shot because the ball can be moved back too much due to back spin. For this reason, the spin factor is preferably in the range between 1.0 and 1.5.

The golf ball of the invention is advantageously applied to two-piece golf balls while it is also applicable to multi-core golf balls such as three-piece golf balls. The material and preparation of the core and cover are not critical. The components may be made of any of well-known materials insofar as the requirements of the invention are met. Of course, the golf ball of the invention has a standard size and weight.

More particularly, the core of the present solid golf ball is formed from a rubber composition by a conventional method while properly adjusting the component proportion and vulcanizing conditions. The core composition generally includes a base rubber, a crosslinking agent, a co-crosslinking agent, an inert filler, and other components. The base rubber may be selected from natural and synthetic rubbers conventionally used in the manufacture of solid golf balls. Preferably the base rubber is 1,4-polybutadiene rubber containing at least 40% of cis-configuration, optionally in admixture with natural rubber, polyisoprene rubber or styrene-butadiene rubber. The crosslinking agent is preferably selected from organic peroxides such as dicumyl peroxide and di-t-butyl peroxide, with the dicumyl peroxide being more preferred. Preferably the crosslinking agent is blended in an amount of about 0.5 to 3 parts, more preferably about 0.8 to 1.5 parts by weight per 100 parts by weight of the base rubber. Non-limiting examples of the co-crosslinking agent include metal salts of unsaturated fatty acids, especially zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms, such as acrylic acid and methacrylic acid. Zinc acrylate is the most preferred salt. The co-crosslinking agent is preferably blended in an amount of about 24 to 38 parts, more preferably about 28 to 34 parts by weight per 100 parts by weight of the base rubber. Examples of the inert filler include zinc oxide, barium sulfate, silica, calcium carbonate, and zinc carbonate, with the zinc oxide being most often used. The amount of the filler blended depends on the desired specific gravity of the core and cover, ball weight, and other factors although it generally ranges from about 10 to about 60 parts by weight per 100 parts by weight of the base rubber.

These components are blended to form a core-forming rubber composition which is kneaded by means of a conventional kneading machine such as a Banbury mixer and

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roll mill and then compression or injection molded in a spherical mold cavity. The molded composition is cured by heating it at a sufficient temperature for the crosslinking and co-crosslinking agents to exert their function (for example, about 130° to 170° C. when the crosslinking agent is dicumyl peroxide and the co-crosslinking agent is zinc acrylate). In this way, a solid spherical core having a diameter of 37 to 40 mm is prepared.

In the case of a two layer core, the inner core may be made of the same composition as above and the outer core may be made of a similar rubber composition or a resin composition based on an ionomer resin or the like. The outer core may be formed by compression molding or injection molding it around the inner core. Typically the inner core has a diameter of 27.0 to 38.0 mm, preferably 28.0 to 36.0 mm and the outer core has a diameter of 0.5 to 6.5 mm, preferably 1.5 to 5.5 mm, and the total diameter ranges from 37 to 40 mm.

The solid core is enclosed with the cover by any desired technique, for example, by enclosing the core in a pair of semi-spherical shell halves followed by heat compression molding. Alternatively the core is directly covered with a cover material by injection molding. By properly selecting the material and amount of the core and cover and preparation conditions such as vulcanizing conditions, a golf ball satisfying the requirements of the invention can be prepared.

There has been described a golf ball which is improved in feel and spin characteristics while maintaining the flying distance inherent to solid golf balls and which undergoes a lower degree of reduction of its flying distance upon hitting at a lower head speed.

#### EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

#### Examples 1-6 and Comparative Examples 1-2

Cores having a hardness as shown in Table 1 were molded by vulcanizing in a mold rubber compositions comprising cis-1,4-polybutadiene rubber, zinc acrylate, zinc oxide, and dicumyl peroxide. The core hardness reported is a distortion in millimeter under a load of 100 kilograms.

The cores were enclosed with covers which were formed from mixtures of ionomer resins. The blending proportion of ionomer resins was changed to form covers having varying hardness (Shore D scale) as shown in Table 2. In this way, there were obtained large-size two-piece golf balls having a hardness as shown in Table 3. The ball hardness reported is again a distortion in millimeter under a load of 100 kilograms.

The base composition for the core consisted of the following components.

Parts by weight	
cis-1,4-polybutadiene rubber (BR01)	100
zinc acrylate	33.2
zinc oxide	10
barium sulfate	9.7
anti-oxidant	0.2
dicumyl peroxide	0.9

Cores having varying hardness and specific gravity were obtained by varying the amounts of zinc acrylate and barium sulfate as shown in Table 1.

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TABLE 1

Core hardness	Cover gage				
	1.4 mm	1.6 mm	1.8 mm	2.0 mm	2.4 mm
2.48-2.50 mm	33.0	33.0	33.0	33.0	
	6.4	7.5	8.6	9.7	
2.88-2.91 mm	31.0	31.0	31.0	31.0	31.0
	7.8	8.8	9.9	11.0	13.9
3.25-3.30 mm	28.0	28.0	28.0	28.0	
	9.1	10.2	11.2	12.3	

At the upper and lower stages for each core hardness and cover gage combination, the amounts of zinc acrylate and barium sulfate are reported in parts by weight, respectively.

The base composition for the cover was a 50/50 (by weight) mixture of ionomer resins, Himilan 1650 and Surlyn

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#### Stop on the Green Test

Using a swing robot manufactured by True Temper Co., the ball was hit by a pitching wedge at a head speed of 35 m/s so as to fly directly on the green. The distance between the landing and stop positions was measured. A negative value is the distance the ball covers due to back spin. A positive value is a run in a flying direction. The stop on the green was rated "O" for quick stop and "X" for non-stopping.

#### 10 Feel Test

In a sensory test, a player hit the ball at a head speed (HS) of 35 m/s. The ball feel was rated "very soft", "soft" or "hard".

Note that the dependency of flying distance on head speed is expressed by the flying distance at a head speed of 35 m/s divided by the flying distance at a head speed of 45 m/s and simply reported under the heading "HS35/HS45" in Table 3.

TABLE 3

	Example						Comparative Example	
	1	2	3	4	5	6	1	2
Core hardness (mm)	2.48	3.30	2.50	2.90	2.91	3.25	2.10	2.85
Ball hardness (mm)	2.36	3.10	2.30	2.71	2.65	2.90	1.90	2.10
Core/ball hardness ratio	1.05	1.06	1.09	1.07	1.10	1.12	1.11	1.36
Cover thickness (mm)	1.4	1.4	1.6	1.6	1.8	1.8	1.8	2.4
Cover hardness (Shore D)	56	57	56	56	56	57	57	65
Feel @ HS35	soft	very soft	soft	very soft	soft	very soft	hard	soft
Flying distance (m)								
@ HS 35	154	160	154	158	157	159	147	148
@ HS 45	234	237	232	233	233	236	228	235
Stop on the green								
Landing-to-stop distance (m)	-0.5	0.5	0.0	0.0	0.0	0.5	0.0	2.5
Rating	o	o	o	o	o	o	o	x
HS35/HS45	0.658	0.675	0.664	0.678	0.674	0.673	0.645	0.630

8120. Covers having varying hardness were obtained while blending Himilan 1650 and Surlyn 8120 in a ratio as shown in Table 2.

TABLE 2

Cover hardness (Shore D)	Resin mix	Weight ratio
56	H1650/S8120	40/60
57	H1650/S8120	50/50
65	H1605/H1706	50/50

\* H: Himilan commercially available from du Pont-Mitsui Polychemical Co., Ltd.  
S: Surlyn commercially available from E. I. duPont

The golf balls were examined for fly, stop on the green, and feel by the following procedures.

#### Fly Test

Using a swing robot manufactured by True Temper Co., the ball was hit by a driver at a head speed (HS) of 45 m/s and by an iron at a head speed of 35 m/s to measure the flying distance.

40 Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

#### We claim:

1. A golf ball comprising a core and a cover wherein said core and said ball has a core hardness and a ball hardness respectively, wherein said core has a distortion of 2.9 to 4.0 mm under a load of 100 kg, the ratio of a core distortion under a load of 100 kg divided by a ball distortion under a load of 100 kg ranges from 1.0 to 1.3, and said cover consists of an ionomer resin as a resin component and has a thickness of 1.3 to 1.8 mm and a Shore D hardness of up to 60.

2. The golf ball of claim 1 wherein said cover has a thickness of 1.6 to 1.8 mm.

\* \* \* \* \*

# EXHIBIT D

(12) **United States Patent**  
**Watanabe**

(10) **Patent No.:** **US 6,679,791 B2**  
(45) **Date of Patent:** **Jan. 20, 2004**

(54) **GOLF BALL**

(75) Inventor: **Hideo Watanabe**, Chichibu (JP)

(73) Assignee: **Bridgestone Sports Co., Ltd.**, Tokyo (JP)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/880,844**

(22) Filed: **Jun. 15, 2001**

(65) **Prior Publication Data**

US 2002/0019269 A1 Feb. 14, 2002

(30) **Foreign Application Priority Data**

Jun. 26, 2000 (JP) ..... 2000-190640

(51) **Int. Cl.<sup>7</sup>** ..... **A63B 37/04**; A63B 37/06; A63B 37/00

(52) **U.S. Cl.** ..... **473/371**; 473/351

(58) **Field of Search** ..... 473/251–377

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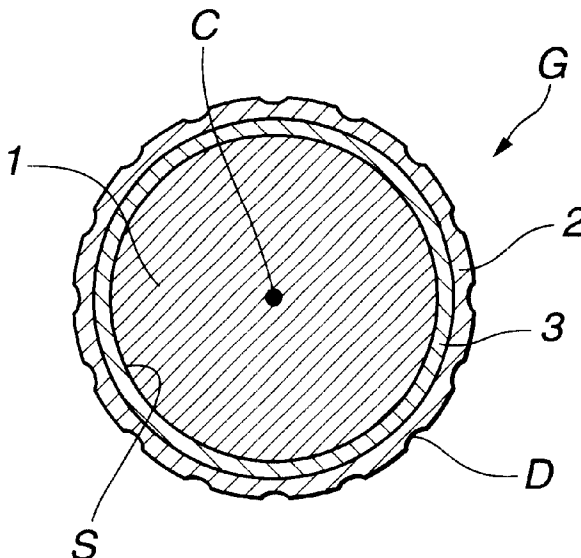
*Assistant Examiner*—Alvin A. Hunter, Jr.

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(57) **ABSTRACT**

A multi-piece golf ball includes a rubbery elastic core, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof. The center and surface of the elastic core have a hardness difference of at least 18 JIS-C hardness units. This construction and combination of features improve the distance of the ball when struck with a driver, provide the ball with excellent spin characteristics and thus good controllability on approach shots, and gives the ball a good feel on impact, enabling the ball to meet the high expectations of skilled golfers.

**27 Claims, 1 Drawing Sheet**

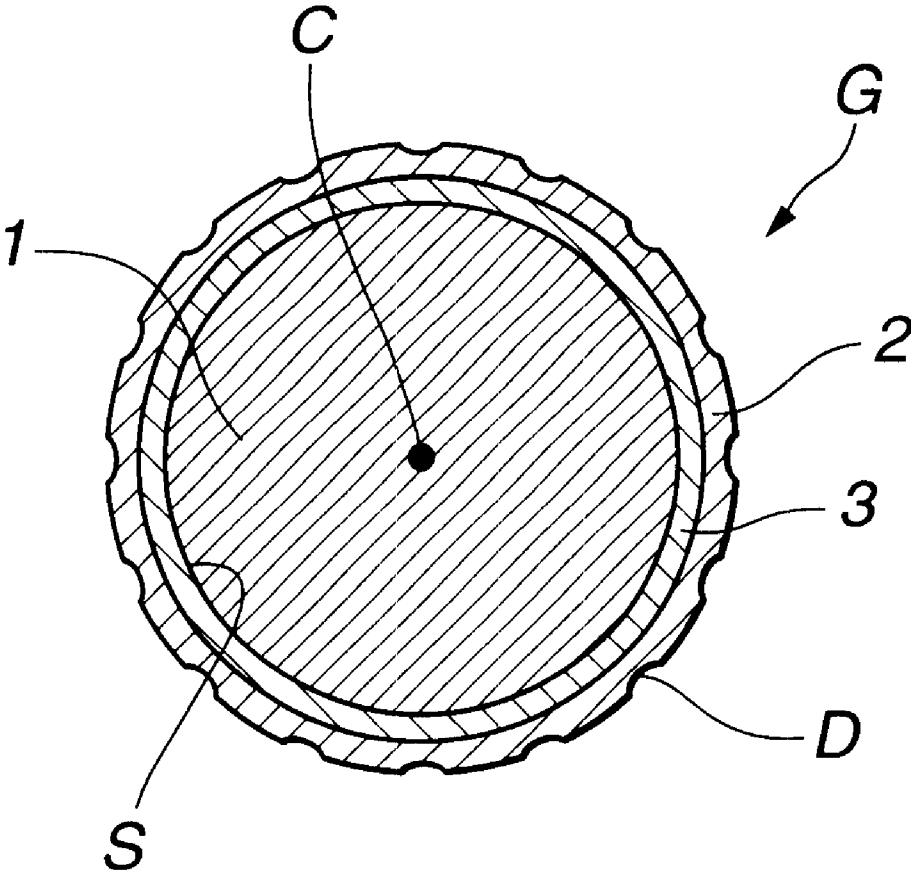


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FIG.1





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**GOLF BALL****BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a golf ball having a multilayer construction of at least three layers which includes a core, an intermediate layer and a cover. More particularly, the invention relates to a golf ball which has good rebound characteristics and provides an excellent travel distance, controllability and "feel" upon impact with a golf club.

**2. Prior Art**

In recent years, solid golf balls, with their good flight performance, have consistently won greater general approval than conventional thread-wound golf balls.

Solid golf ball constructions include two-piece balls made of a solid, high-resilience, rubber core enclosed within a relatively thin resin cover, and multi-piece balls having a core, a cover, and also an intermediate layer therebetween whose properties differ somewhat from those of the cover.

As already noted, because of their good flight performance (i.e., long travel distance), solid golf balls of these types are widely favored by both amateur and professional golfers. Yet, there remains a desire among golfers for even better flight performance.

**SUMMARY OF THE INVENTION**

It is therefore an object of the present invention to provide a golf ball having a multilayer construction of three or more layers that is endowed with improved distance without diminishing the controllability and feel that are so important to skilled golfers.

Accordingly, the invention provides a golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof, and a difference in JIS-C hardness of at least 18 between the center and the surface.

Preferably, the JIS-C hardness at the center of the core is 50 to 65, and the JIS-C hardness at the surface of the core is 70 to 90. The core typically undergoes a deformation of 3.0 to 5.0 mm when the load applied thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf).

**BRIEF DESCRIPTION OF THE DRAWING**

The objects, features and advantages of the invention will become more apparent from the following detailed description, taken in conjunction with the accompanying diagram.

The only FIGURE, FIG. 1 is a sectional view showing a golf ball according to one embodiment of the invention.

**DETAILED DESCRIPTION OF THE INVENTION**

Referring to FIG. 1, the golf ball G of the present invention has a construction composed of at least three layers, commonly known as a "multi-piece construction," which include a rubbery elastic core 1, a cover 2 that is

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generally made of a resin material and has a plurality of dimples D on the surface thereof, and one or more intermediate layer 3 between the core 1 and the cover 2, all situated in a concentric fashion. The illustrated embodiment has a single intermediate layer. The intermediate layer 3 is made of a resin material which is harder than the cover 2. The core 1 having a center C and a surface S at its radially outer extremity has a JIS-C hardness which gradually increases radially outward from the center C to the surface S. The core 1 is formed so as to have a specific hardness difference between the surface S and the center C.

The inventive golf ball includes a hard intermediate layer disposed between the core, which has an optimized hardness profile, and the cover which is softer than the intermediate layer. This construction provides the ball with an excellent "feel," holds down spin when the ball is struck with a driver, and increases the distance traveled, in part by creating a trajectory which does not describe a high arc when traveling into a headwind. At the same time, it increases the amount of spin on approach shots taken with a club having a large loft angle, thus imparting the excellent control desired in particular by professionals and other skilled golfers.

In the golf ball of the present invention, the core may be made from a known core material which is prepared by blending, for example, a base rubber, the metal salt of an unsaturated carboxylic acid, and an organic peroxide.

The base rubber is preferably polybutadiene. The use of 1,4-polybutadiene, and especially one having a cis structure of at least 40%, is recommended. In addition to the polybutadiene, the base rubber may also include other rubbers such as natural rubber, polyisoprene rubber and styrene-butadiene rubber, if necessary.

Examples of suitable metal salts of unsaturated carboxylic acids include zinc dimethacrylate and zinc diacrylate. Zinc diacrylate is especially preferred for achieving a high rebound energy. It is advantageous to include such unsaturated carboxylic acids in an amount of at least 15 parts by weight, and preferably at least 20 parts by weight, but not more than 50 parts by weight, and preferably not more than 45 parts by weight, per 100 parts by weight of the base rubber.

Examples of suitable organic peroxides include 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-(t-butylperoxy)-m-diisopropylbenzene and 2,5-dimethyl-2,5-di-t-butylperoxyhexane. It is advantageous to include such peroxides in an amount of at least 0.1 part by weight, and preferably at least 0.5 part by weight, but not more than 5 parts by weight, and preferably not more than 2 parts by weight, per 100 parts by weight of the base rubber.

To impart good rebound characteristics, it is advisable to include a suitable compounding ingredient such as a thiophenol, thionaphthol, halogenated thiophenol or metal salt thereof in the core material. Specific examples of such compounding ingredients that may be used include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol. The zinc salt of pentachloro-thiophenol is especially preferred. Such a compounding ingredient is typically included in an amount of at least 0.4 part by weight, and preferably at least 0.6 part by weight, but not more than 2.0 parts by weight, and preferably not more than 1.2 parts by weight, per 100 parts by weight of the base rubber. Too much of this ingredient tends to lower the core hardness, which can adversely impact the feel of the ball when hit as well as its durability (cracking resistance), whereas too little may lower the rebound energy of the core, making it impossible for the ball to achieve a sufficient carry.

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If necessary, the core material may include also various additives such as inorganic fillers and antioxidants. Illustrative examples of such additives include zinc oxide, barium sulfate and calcium carbonate.

The core may be fabricated from the above core material by using a conventional process to blend the various ingredients and mold the resulting mixture. For example, the constituent ingredients may be blended in a suitable apparatus such as a Banbury mixer or a kneader to form a "slug," which is then placed in a mold where it is vulcanized at a temperature of generally at least 150° C., and preferably at least 160° C., but generally not more than 190° C., and preferably not more than 180° C. The period of vulcanization is generally at least 8 minutes, and preferably at least 12 minutes, but generally not more than 20 minutes, and preferably not more than 16 minutes.

The weight and diameter of the core may be suitably adjusted according to such factors as the constituent materials and thickness of the intermediate layer and the cover, which are described subsequently. It is recommended that the core generally have a weight of at least 23 g, and preferably at least 30 g, but not more than 37 g, and preferably not more than 35 g. It is also recommended that the core generally have a diameter of at least 33 mm, and preferably at least 36 mm, but not more than 39 mm, and preferably not more than 38 mm.

It is critical for the core to have an optimized hardness profile in which the hardness gradually increases radially outward from the center toward the outside edge or surface of the core. That is, the core has a higher hardness at the surface than at the center.

The core center and surface must have a difference between their respective measured JIS-C hardnesses of at least 18, preferably at least 20, and most preferably at least 22 units. This difference in hardness within the core gives the ball a low spin when hit with a driver (number 1 wood), enabling it to travel well and thus attain a good total distance. Too small a difference in JIS-C hardness between the relatively soft center and the relatively hard surface of the core allows the ball to take on too much spin when hit with a driver, so that it does not travel well and has a short run after it lands on the ground. This makes it impossible to achieve the desired distance. It is recommended that the upper limit in the hardness difference be at most 30, preferably 27 or less, and most preferably 25 units or less.

Specifically, the core at the center typically has a JIS-C hardness of at least 50, and preferably at least 55, but not more than 65, and preferably not more than 62. The core at the surface typically has a JIS-C hardness of at least 70, and preferably at least 75, but not more than 90, and preferably not more than 85. Too low a JIS-C hardness at the core center may deaden the feel and fail to achieve the desired rebound energy, whereas a hardness that is too high may result in an excessively hard feel when the ball is hit. Similarly, too low a JIS-C hardness at the core surface may deaden the feel of the ball when hit, while too high a hardness may result in too hard a feel.

Preferably the core of the inventive golf ball has a deformation of at least 3.0 mm, and preferably at least 3.3 mm, but not more than 5.0 mm, and preferably not more than 4.5 mm, when the load applied thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf). Too small a deformation may increase the spin when the ball is hit with a driver, preventing the desired travel from being achieved, and may also give the ball too hard a feel. On the other hand, too much deformation may deaden the feel and fail to achieve the necessary rebound energy.

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Since the core has a hardness gradually increasing radially outward from the center to the surface thereof and an optimized difference in hardness between the center and the surface where the core is hardest, the inventive golf ball having the above-described core functions to suppress the generation of excessive spin when it is hit with a driver, effectively increasing the run after it lands on the ground, and thus travelling a longer total distance.

The intermediate layer **3** of the inventive golf ball is an essential layer which is situated between the core **1** and the cover **2** of the ball **G**, as shown in FIG. 1, and is made of a resin material that is harder than the cover material. Even if the core and cover are within the scope of the present invention, a golf ball lacking the adequate intermediate layer prescribed by the present invention fails to attained the objects of the invention since it cannot adequately suppress spin when hit with a driver, making it impossible to achieve a longer travel distance, and gives a poor feel when hit.

The intermediate layer may be made using a known cover material, illustrative examples of which include an ionomer resin, either by itself or in admixture with a polyester, polyurethane, polyamide, polyolefin or polystyrene thermoplastic elastomer. The use of an ionomer resin by itself is especially preferred, although another thermoplastic resin may be used provided the resin material for the intermediate layer has a greater hardness than the cover. As with the cover material described below, pigments and various other additives may be included in the intermediate material.

The intermediate layer can be formed over the surface of the core using a known process, preferably an injection molding process. For example, once the core is placed within a mold, the intermediate layer material is injection molded over the core in a conventional manner.

The intermediate layer must have a greater hardness than the cover, which is described below. If the intermediate layer has a hardness which is the same as or lower than that of the cover, spin is not adequately suppressed when the ball is hit with a driver, in addition to which the ball has a lower rebound energy, preventing the anticipated total distance from being achieved. It is generally advantageous for the intermediate layer and the cover to have a Shore D hardness difference of at least 2, and preferably at least 5 units, but not more than 20, and preferably not more than 15 units.

It is recommended that the intermediate layer itself have a Shore D hardness of generally at least 50, and preferably at least 55, but not more than 67, and preferably not more than 65.

As already noted, the intermediate layer situated between the core and the cover in the golf ball of the invention has a greater hardness than the cover. The hardnesses of the intermediate layer and the core, when compared using the same hardness scale (i.e., JIS-C hardness or Shore D hardness), are preferably such that the intermediate layer has a greater hardness than the surface of the core. The JIS-C hardness difference between the intermediate layer and the core surface is preferably at least 2, and more preferably at least 6 units, but not more than 22, and more preferably not more than 18 units.

It is recommended that the intermediate layer have a thickness which is generally at least 0.5 mm, but not more than 3 mm, and especially not more than 2 mm. In cases where there are two or more intermediate layers, it is advisable to set the overall thickness of the intermediate layers within the above range.

If the golf ball has two or more intermediate layers situated between the core and the cover, the above-described



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hardness relationship must be maintained between the cover and the outer intermediate layer which is in close contact with the cover.

The cover of the golf ball is formed of a material which is softer than the intermediate layer material. Examples of suitable cover materials include ionomer resins and polyurethane thermoplastic elastomers which are softer than the intermediate layer material. The use of an ionomer resin is especially preferred.

It is advantageous for the cover to have a Shore D hardness of generally at least 45, and especially at least 48, but not more than 60, and especially not more than 58. A hardness value that is too low may result in increased spin and an inability to achieve the required total distance. On the other hand, a hardness value that is too high may adversely impact the controllability of shots taken with an iron club having a large loft angle, and approach shots.

A conventional process may be used to form the cover. It is especially preferable to use an injection molding process in which a solid core over which an intermediate layer has been formed is placed within a mold, and the cover material is injection molded over the intermediate layer.

It is recommended that the cover generally have a thickness of at least 0.6 mm, and preferably at least 1.0 mm, but not more than 2.1 mm, and preferably not more than 1.8 mm. Too thin a cover may lower the durability of the ball, whereas a cover that is too thick may lower the ball's rebound energy.

Since the golf ball of the invention has an optimized balance in hardness among the various layers as described above, the ball is endowed with an excellent rebound energy, distance performance, feel, controllability and spin characteristics.

For competition play, the golf ball of the invention may be formed so as to have a diameter and weight which conform with the Rules of Golf. That is, the ball may have a diameter of not less than 42.67 mm and a weight of not greater than 45.93 g.

The inventive golf ball provides increased distance when hit with a driver. On approach shots, the ball has excellent spin characteristics to ensure control as desired. Moreover, it has a good feel on impact. This combination of qualities enables the ball to satisfy the high expectations of skilled golfers in particular.

EXAMPLES

Examples of the invention and comparative examples are given below by way of illustration, and are not intended to limit the invention.

Examples 1-3 and Comparative Examples 1-5

To ascertain the flight characteristics and feel of golf balls according to one embodiment of the invention, golf balls

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with different hardnesses at the center and surface of the core were produced in Examples 1, 2 and 3. A number of additional examples were carried out for the purpose of comparison. The golf balls produced in Comparative Example 1 had cores with a small or flat hardness profile. The balls produced in Comparative Example 2 had cores with a noticeable, yet gradual, hardness profile. The balls produced in Comparative Example 3 had a core with a distinct hardness profile, but had an intermediate layer that was softer than the cover. The balls produced in Comparative Examples 4 and 5 similarly had cores with distinct hardness profiles, but lacked an intermediate layer. Comparative tests were conducted on these various balls.

The balls were all given the same arrangement of dimples on the surface of the cover. Namely, each ball had a total of 432 dimples of three types formed on the cover in an icosahedral arrangement.

Tables 1 and 2 below show the characteristics of the cover and intermediate layer in the ball samples in each example. Table 3 gives the characteristics of the core in the same balls, and Table 4 presents the test results obtained for each type of ball.

TABLE 1

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Cover	Material	a	a	a	a	a	b	a	a
	Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Hardness (Shore D)	55	55	55	55	55	65	55	55
Intermediate layer	Material	b	b	b	b	b	a	—	—
	Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	—	—
	Hardness (Shore D)	65	65	65	65	65	55	—	—

TABLE 2

		Cover, intermediate layer		a	b
Composition (parts by weight)	Himilan AM7317 (Zn) <sup>1)</sup>				50
	Himilan 1650 (Zn) <sup>2)</sup>			50	
	Himilan AM7318 (Na) <sup>3)</sup>				50
	Surlyn 8120 (Na) <sup>4)</sup>			50	
Hardness	Titanium oxide			5	5
	Shore D hardness			55	65
	JIS-C hardness			80	94

<sup>1)</sup>A zinc ionomer resin having an acid content of 18% made by DuPont-Mitsui Polychemicals Co., Ltd.

<sup>2)</sup>A zinc ionomer resin made by DuPont-Mitsui Polychemicals Co., Ltd.

<sup>3)</sup>A sodium ionomer resin having an acid content of 18% made by DuPont-Mitsui Polychemicals Co., Ltd.

<sup>4)</sup>A sodium ionomer resin made by E. I. DuPont de Nemours and Co.

TABLE 3

			Example			Comparative Example				
			1	2	3	1	2	3	4	5
Core	Composition (pbw)	1,4-cis-Polybutadiene	100	100	100	100	100	100	100	100
		Zinc diacrylate	41.0	38.0	35.0	28.0	27.8	38.0	32.1	28.4
		Peroxide (1) <sup>1)</sup>	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
		Peroxide (2) <sup>2)</sup>	0.8	0.8	0.8	0.6	0.6	0.8	0.8	0.8
		Sulfur <sup>3)</sup>	0.1	0.1	0.1	0	0	0.1	0.1	0.1
		Antioxidant <sup>4)</sup>	0	0	0	0.2	0.2	0	0	0
		Barium sulfate	24.1	25.2	26.4	29.8	29.9	25.2	12.8	14.4
		Zinc oxide	5	5	5	5	5	5	5	5

TABLE 3-continued

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Vulcanization conditions	Zinc salt of pentachlorothiophenol	1	1	1	0.2	0.2	1	1	1
	Primary Temperature (° C.)	175	175	175	140	155	175	175	175
	Time (min)	15	15	15	30	15	15	15	15
	Secondary Temperature (° C.)	—	—	—	165	—	—	—	—
Hardness	Time (min)	—	—	—	15	—	—	—	—
	Surface (JIS-C hardness)	85	83	78	76	76	83	87	80
	Center (JIS-C hardness)	61	59	55	72	60	59	63	56
	JIS-C hardness difference	24	24	23	4	16	24	24	24
Deformation under loading (mm) <sup>5)</sup>		3.4	3.8	4.1	3.3	3.4	3.8	3.4	4.1

<sup>1)</sup>Dicumyl peroxide, produced by NOF Corporation under the trade name Percumyl D.  
<sup>2)</sup>1,1-Bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, produced by NOF Corporation under the trade name Perhexa 3M-40.  
<sup>3)</sup>Zinc white-containing sulfur, produced by Tsurumi Chemical Industry Co., Ltd.  
<sup>4)</sup>Nocrack NS-6, produced by Ouchi Shinko Chemical Industrial Co., Ltd.  
<sup>5)</sup>Deformation under loading from an initial load of 98 N to a final load of 1,275 N.

TABLE 4

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Flight <sup>1)</sup>	Carry (m)	233.0	232.2	231.1	233.2	232.1	232.5	231.8	229.5
	Total distance (m)	241.2	243.8	244.9	238.5	239.9	245.5	238.3	241.1
	Spin (rpm)	2805	2745	2700	2910	2855	2550	2952	2847
	Rating	good	good	good	poor	poor	good	poor	fair
Approach <sup>2)</sup>	Spin (rpm)	5833	5821	5811	5849	5830	4100	5870	5832
	Rating	good	good	good	good	good	poor	good	good
Feel <sup>3)</sup>	When hit with driver	good	good	good	good	good	good	good	poor
	When hit with putter	good	good	good	good	good	poor	good	good

<sup>1)</sup>Flight was rated as follows, based on distance measured when ball was hit at a head speed of 50 m/s by a driver mounted on a swing robot.  
Good: Total distance at least 241 m  
Fair: Total distance at least 241 m, but carry less than 230 m  
Poor: Total distance 240 m or less.  
<sup>2)</sup>Approach was rated as follows, based on spin rate measured when ball was hit at a head speed of 19 m/s by a sand wedge mounted on a swing robot.  
Good: Good spin (at least 5,500 rpm)  
Poor: Inadequate spin (less than 4,500 rpm)  
<sup>3)</sup>Average sensory evaluations for five professional golfers:  
Good: Feel was appropriate and good.  
Poor: Feel was too hard or too soft.

As is apparent from the results in Table 4, the golf balls according to the invention all showed a good balance of distance, controllability on approach shots, and feel. By contrast, the golf balls produced in the comparative examples each had drawbacks. In Comparative Examples 1 and 2, the hardness difference between the surface and center of the core was less than 18, resulting in much spin and a poor distance when the ball was hit with a driver. In Comparative Example 3, the cover was harder than the intermediate layer, and had an excessively high hardness. As a result, the amount of spin on approach shots was low and controllability was poor. In addition, the feel when hit with a putter was poor. The golf balls produced in Comparative Example 4 were two-piece balls which lacked between the cover and the core an intermediate layer of greater hardness than the cover. These balls had a lot of spin when hit with a driver, and thus a poor distance. In the golf balls produced in Comparative Example 5, the core hardness was lowered to reduce the high spin rate on impact with a driver in Comparative Example 4, but the resulting feel on impact with a driver was too soft. Japanese Patent Application No. 2000-190640 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein said intermediate layer is composed of a resin material which is harder than the cover and has a greater hardness than the surface of the elastic core when compared using the same hardness scale, and said elastic core has a hardness which gradually increases radially outward from the center to the surface thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

2. The golf ball of claim 1, wherein said core at the center has a JIS-C hardness of 50 to 65, and at the surface a JIS-C hardness of 70 to 90.

3. The golf ball of claim 1, wherein said core undergoes a deformation of 3.0 to 5.0 mm when the load applied

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thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf).

4. The golf ball of claim 1, wherein the difference in JIS-C hardness between the center of the elastic core and the surface thereof is 22 to 30 units.

5. The golf ball of claim 1, wherein the intermediate layer has a Shore D hardness of 50 to 67.

6. The golf ball of claim 1, wherein the JIS-C hardness difference between said intermediate layer and said core surface is 2 to 22 units.

7. The golf ball of claim 1, wherein the cover has a Shore D hardness of 45 to 60.

8. The golf ball of claim 1, wherein the golf ball has two or more intermediate layers situated between the core and the cover, and said hardness relationship is maintained between the cover and the outer intermediate layer which is in close contact with the cover.

9. The golf ball of claim 1, wherein the core is formed of rubber as a base and the cover is formed of materials including ionomer resins and polyurethane thermoplastic elastomers.

10. The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

11. The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol.

12. The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

13. A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover, and has a greater hardness than the surface of the elastic core when compared using the same JIS-C hardness scale, and

said elastic core has a hardness at the center and a hardness at the surface thereof which is greater than the hardness at the center thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

14. The golf ball of claim 13, wherein said core at the center has a JIS-C hardness of 50 to 65, and at the surface a JIS-C hardness of 70 to 90.

15. The golf ball of claim 13, wherein the difference in JIS-C hardness between the center of the elastic core and the surface thereof is 22 to 30 units.

16. The golf ball of claim 13, wherein the intermediate layer has a Shore D hardness of 50 to 67.

17. The golf ball of claim 12, wherein the JIS-C hardness difference between said intermediate layer and said core surface is 2 to 22 units.

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18. The golf ball of claim 12, wherein the cover has a Shore D hardness of 45 to 60.

19. The golf ball of claim 12, wherein the golf ball has two or more intermediate layers situated between the core and the cover, and said hardness relationship is maintained between the cover and the outer intermediate layer which is in close contact with the cover.

20. The golf ball of claim 12, wherein the core is formed of rubber as a base and the cover is formed of materials including ionomer resins and polyurethane thermoplastic elastomers.

21. The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

22. The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentafluorothiophenol.

23. The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

24. A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover having a Shore D hardness of 45 to 58 and has a greater hardness than the surface of the elastic core when compared using the same hardness scale, and

said elastic core has a hardness at the center and a hardness at the surface thereof which is greater than the hardness at the center thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

25. The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

26. The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol.

27. The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

\* \* \* \* \*

# EXHIBIT E

(12) **United States Patent**  
**Higuchi et al.**

(10) **Patent No.:** **US 6,634,961 B2**  
(45) **Date of Patent:** **\*Oct. 21, 2003**

- (54) **MULTI-PIECE SOLID GOLF BALL**
- (75) Inventors: **Hiroshi Higuchi**, Chichibu (JP);  
**Atsushi Nanba**, Chichibu (JP)
- (73) Assignee: **Bridgestone Sports Co., Ltd.**, Tokyo (JP)
- (\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.
- This patent is subject to a terminal disclaimer.

- (21) Appl. No.: **10/156,950**
- (22) Filed: **May 30, 2002**
- (65) **Prior Publication Data**

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- (57) **ABSTRACT**

In a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, the solid core is molded from a rubber composition comprising a base rubber composed of (a) 20–100 wt % of a polybutadiene having a high cis-1,4 content, a minimal 1,2 vinyl content and a viscosity  $\eta$  of up to 600 mPa·s at 25° C as a 5 wt % toluene solution, and satisfying a certain relationship between Mooney viscosity and polydispersity index in combination with (b) 0–80 wt % of another diene rubber, (c) an unsaturated carboxylic acid, (d) an organosulfur compound, (e) an inorganic filler, and (f) an organic peroxide; and the outer cover layer has a lower Shore D hardness than the inner cover layer. This combination of features gives the ball a good, soft feel upon impact and an excellent spin performance that provides increased distance.

**9 Claims, No Drawings**

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**MULTI-PIECE SOLID GOLF BALL****BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a multi-piece solid golf ball which has been imparted with a good, soft feel upon impact and an excellent spin performance that makes it possible to achieve an increased distance.

**2. Prior Art**

Various improvements are being made in formulating the polybutadiene used as the base rubber in golf balls so as to confer the balls with outstanding rebound characteristics.

For example, JP-A 62-89750 describes rubber compositions for use as the base rubber in solid golf balls, which compositions are arrived at by blending a polybutadiene having a Mooney viscosity of 70 to 100 and synthesized using a nickel or cobalt catalyst with another polybutadiene having a Mooney viscosity of 30 to 90 and synthesized using a lanthanide catalyst or polybutadiene having a Mooney viscosity of 20 to 50 and synthesized using a nickel or cobalt catalyst.

However, further improvements in the materials are required in the above art to achieve golf balls endowed with a good, soft feel upon impact and an excellent spin performance that helps increase the distance the ball travels when played.

JP-A 2-268778 describes golf balls molded using a blend composed of a polybutadiene having a Mooney viscosity of less than 50 and synthesized using a Group VIII catalyst in combination with a polybutadiene having a Mooney viscosity of less than 50 and synthesized with a lanthanide catalyst. However, golf balls with a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball cannot be obtained in this way.

The existing art also teaches multi-piece solid golf balls in which an intermediate layer is molded of a low-Mooney viscosity polybutadiene (JP-A 11-70187), solid golf balls molded from rubber compositions comprising a polybutadiene having a Mooney viscosity of 50 to 69 and synthesized using a nickel or cobalt catalyst in combination with a polybutadiene having a Mooney viscosity of 20 to 90 and synthesized using a lanthanide catalyst (JP-A 11-319148), solid golf balls molded from compositions based on a rubber having a 1,2 vinyl content of at most 2.0% and a weight-average molecular weight to number-average molecular weight ratio  $M_w/M_n$  of not more than 3.5 (JP-A 11-164912), golf balls molded from rubber compositions containing a high Mooney viscosity polybutadiene (JP-A 63-275356), and golf balls molded from rubber compositions comprising polybutadiene having a high number-average molecular weight in admixture with polybutadiene having a low number-average molecular weight (JP-A 3-151985). However, none of these prior-art golf balls truly have a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball.

Golf balls having a cover composed of a relatively hard inner layer and a relatively soft outer layer have already been disclosed in JP-A 6-218078, JP-A 6-343718, JP-A 7-24085, JP-A 9-239068, JP-A 10-151226, JP-A 10-201880, JP-A 11-104273, JP-A 11-104271, and Japanese Patent Applications No. 2000-274807 and 2000-274843. However, further improvements in distance are desired for the golf balls described in all of these specifications.

**SUMMARY OF THE INVENTION**

It is therefore an object of the present invention to provide multi-piece solid golf balls which are endowed with a good,

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soft feel when hit with a golf club and an excellent spin performance that helps increase the distance traveled by the ball when played.

The inventor has discovered that golf balls having a solid core, an inner cover layer over the cover, and an outer cover layer over the inner cover layer, wherein the solid core is made of a rubber composition formulated from a particular type of base rubber combined in specific proportions with certain other materials, and the outer cover layer is softer than the inner cover layer, exhibit a good synergy from optimization of the solid core materials and an appropriate distribution of hardness between the inner and outer cover layers. Multi-piece solid golf balls thus constituted have a good, soft feel when hit with a golf club and an excellent spin performance that enables the ball to travel further when played.

Accordingly, the invention provides a multi-piece solid golf ball having a solid core, an inner cover layer enclosing the core, and an outer cover layer enclosing the inner cover layer. The solid core is molded from a rubber composition comprising 100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, and satisfying the relationship:  $10B + 5 \leq A \leq 10B + 60$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio  $M_w/M_n$  between the weight-average molecular weight  $M_w$  and the number-average molecular weight  $M_n$  of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a). The rubber composition includes also (c) 10 to 60 parts by weight of an unsaturated carboxylic acid and/or a metal salt thereof, (d) 0.1 to 5 parts by weight of an organosulfur compound, (e) 5 to 80 parts by weight of an inorganic filler, and (f) 0.1 to 5 parts by weight of an organic peroxide. The outer cover layer has a lower Shore D hardness than the inner cover layer.

The polybutadiene (a) is typically synthesized using a rare-earth catalyst.

Preferably, the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of not more than 55, and satisfies the relationship  $\eta \leq 20A - 550$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene and  $\eta$  is the viscosity, in mPa·s, of the second polybutadiene at 25° C. as a 5 wt % solution in toluene. The second polybutadiene in component (b) is typically synthesized using a Group VIII catalyst.

In the multi-piece solid golf ball of the invention, it is generally advantageous for the inner cover layer to have a Shore D hardness of 50 to 80 and the outer cover layer to have a Shore D hardness of 35 to 60.

**DETAILED DESCRIPTION OF THE INVENTION**

The golf ball of the invention includes a solid core made of a rubber composition in which the base rubber is at least partly polybutadiene. It is critical that the base rubber contain as component (a) a specific amount of a polybutadiene in which the cis-1,4 and 1,2 vinyl contents, the viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene, and the relationship between the Mooney viscosity and the polydispersity index  $M_w/M_n$  have each been optimized.

That is, the polybutadiene (a) has a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least



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90%, and most preferably at least 95%; and has a 1,2 vinyl content of at most 2%, preferably at most 1.7%, more preferably at most 1.5%, and most preferably at most 1.3%. Outside of the above ranges, the resilience declines.

The polybutadiene (a) must also have a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s. "Viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene" refers herein to the value in mPa·s units obtained by dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene and carrying out measurement with a specified viscometer at 25° C. using a standard solution for the viscometer (JIS Z8809).

The polybutadiene (a) has a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s, preferably not more than 550 mPa·s, more preferably not more than 500 mPa·s, even more preferably not more than 450 mPa·s, and most preferably not more than 400 mPa·s. Too high a viscosity  $\eta$  lowers the workability of the rubber composition. It is recommended that the viscosity  $\eta$  be at least 50 mPa·s, preferably at least 100 mPa·s, more preferably at least 150 mPa·s, and most preferably at least 200 mPa·s. Too low a viscosity  $\eta$  may lower the resilience.

In addition, the polybutadiene (a) must satisfy the relationship:

$$10B+5 \leq A \leq 10B+60,$$

wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene. A is preferably at least 10B+7, more preferably at least 10B+8 and most preferably at least 10B+9, but preferably not more than 10B+55, more preferably not more than 10B+50, and most preferably not more than 10B+45. If A is too low, the resilience declines. On the other hand, if A is too high, the workability of the rubber composition worsens.

It is recommended that the polybutadiene (a) have a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of at least 20, preferably at least 30, more preferably at least 40, and most preferably at least 50, but not more than 80, preferably not more than 70, more preferably not more than 65, and most preferably not more than 60.

The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol  $ML_{1+4}$  (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

It is desirable for the polybutadiene (a) to be synthesized using a rare-earth catalyst. A known rare-earth catalyst may be used for this purpose.

Examples of suitable catalysts include lanthanide series rare-earth compounds, organoaluminum compounds, alumoxane, halogen-bearing compounds, optionally in combination with Lewis bases.

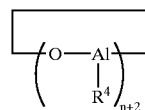
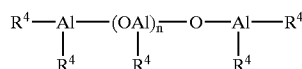
Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals.

Organoaluminum compounds that may be used include those of the formula  $AlR^1R^2R^3$  (wherein  $R^1$ ,  $R^2$  and  $R^3$  are

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each independently a hydrogen or a hydrocarbon residue of 1 to 8 carbons).

Preferred alumoxanes include compounds of the structures shown in formulas (I) and (II) below. The alumoxane association complexes described in *Fine Chemical* 23, No. 9, 5 (1994), *J. Am. Chem. Soc.* 115, 4971 (1993), and *J. Am. Chem. Soc.* 117, 6465 (1995) are also acceptable.



In the above formulas,  $R^4$  is a hydrocarbon group having 1 to 20 carbon atoms, and n is 2 or a larger integer.

Examples of halogen-bearing compounds that may be used include aluminum halides of the formula  $AlX_nR_{3-n}$  (wherein X is a halogen; R is a hydrocarbon residue of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as  $Me_3SrCl$ ,  $Me_2SrCl_2$ ,  $MeSrHCl_2$  and  $MeSrCl_3$  (wherein "Me" stands for methyl); and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride.

The Lewis base may be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols.

In the practice of the invention, the use of a neodymium catalyst composed in part of a neodymium compound as the lanthanide series rare-earth compound is advantageous because it enables a polybutadiene rubber having a high cis-1,4 content and a low 1,2 vinyl content to be obtained at an excellent polymerization activity. Preferred examples of such rare-earth catalysts include those mentioned in JP-A 11-35633.

The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature in a range of generally -30° C. to +150° C., and preferably 10° C. to 100° C.

It is also possible for the polybutadiene (a) to be obtained by polymerization using the above-described rare-earth catalyst, followed by the reaction of an end group modifier with active end groups on the polymer.

Any known end group modifier may be used. Examples include compounds of types (1) to (6) described below:

(1) halogenated organometallic compounds, halogenated metallic compounds and organometallic compounds of the general formulas  $R^5_nM^iX_{4-n}$ ,  $M^iX_4$ ,  $M^iX_3$ ,  $R^5_nM^i(-R^6-COOR^7)_{4-n}$  or  $R^5_nM^i(-R^6-COR^7)_{4-n}$  (wherein  $R^5$  and  $R^6$  are each independently a hydrocarbon group of 1 to 20 carbons;  $R^7$  is a hydrocarbon group of 1 to 20 carbons which may contain a carbonyl or ester moiety as a side chain;  $M^i$  is a tin atom, silicon atom, germanium atom or phosphorus atom; X is a halogen atom; and n is an integer from 0 to 3);

(2) heterocumulene compounds containing on the molecule a  $Y=C=Z$  linkage (wherein Y is a carbon atom, oxygen atom, nitrogen atom or sulfur atom; and Z is an oxygen atom, nitrogen atom or sulfur atom);

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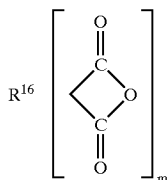
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- (3) three-membered heterocyclic compounds containing on the molecule the following bonds



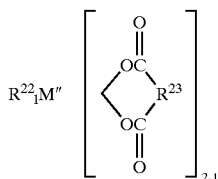
(wherein Y is an oxygen atom, a nitrogen atom or a sulfur atom);

- (4) halogenated isocyano compounds;
- (5) carboxylic acids, acid halides, ester compounds, carbonate compounds or acid anhydrides of the formulas  $R^8-(COOH)_m$ ,  $R^9(COX)_m$ ,  $R^{10}-(COO-R^{11})$ ,  $R^{12}-OCOO-R^{13}$ ,  $R^{14}-(COOCO-R^{15})_m$  or the following formula



(wherein  $R^8$  to  $R^{16}$  are each independently a hydrocarbon group of 1 to 50 carbons; X is a halogen atom; and m is an integer from 1 to 5); and

- (6) carboxylic acid metal salts of the formula  $R^{17}_1M''(OCOR^{18})_{4-1}$ ,  $R^{19}_1M''(OCO-R^{20}-COOR^{21})_{4-1}$  or the following formula



(wherein  $R^{17}$  to  $R^{23}$  are each independently a hydrocarbon group of 1 to 20 carbons,  $M''$  is a tin atom, a silicon atom or a germanium atom; and 1 is an integer from 0 to 3).

Illustrative examples of the end group modifiers of types (1) to (6) above and methods for their reaction are described in, for instance, JP-A 11-35633 and JP-A 7-268132.

In the practice of the invention, component (a) is included in the base rubber in an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, and most preferably at least 35 wt %. The upper limit is 100 wt %, preferably not more than 90 wt %, more preferably not more than 80 wt %, and most preferably not more than 70 wt %.

In addition to component (a), the base rubber may include also a diene rubber (b) insofar as the objects of the invention are attainable. Specific examples of the diene rubbers (b) include polybutadiene rubber, styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDM). Any one or combination of two or more thereof may be used.

The diene rubber (b) is included together with component (a) in the base rubber in an amount of at least 0 wt %, preferably at least 10 wt %, more preferably at least 20 wt %, and most preferably at least 30 wt %, but not more than 80 wt %, preferably not more than 75 wt %, more preferably not more than 70 wt %, and most preferably not more than 65 wt %.

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In the practice of the invention, it is preferable for component (b) to include a polybutadiene rubber, and especially one for which the cis-1,4 and 1,2 vinyl contents, the Mooney viscosity, and the relationship between the Mooney viscosity and  $\eta$  have each been optimized. The polybutadiene serving as component (b) is referred to as "second polybutadiene" in order to distinguish it from the polybutadiene serving as component (a).

It is recommended that the second polybutadiene in component (b) have a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least 90%, and most preferably at least 95%, and that it have a 1,2 vinyl content of at most 5%, preferably at most 4.5%, more preferably at most 4.0%, and most preferably at most 3.5%.

It is recommended that the second polybutadiene have a Mooney viscosity of at least 10, preferably at least 20, more preferably at least 25, and most preferably at least 30, but not more than 55, preferably not more than 50, and most preferably not more than 45.

In the practice of the invention, it is recommended that the second polybutadiene be one that has been synthesized using a Group VIII catalyst. Exemplary Group VIII catalysts include nickel catalysts and cobalt catalysts.

Examples of suitable nickel catalysts include single-component systems such as nickel-kieselguhr, binary systems such as Raney nickel/titanium tetrachloride, and ternary systems such as nickel compound/organometallic compound/boron trifluoride etherate. Exemplary nickel compounds include reduced nickel on a carrier, Raney nickel, nickel oxide, nickel carboxylate and organonickel complexes. Exemplary organometallic compounds include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum and tri-n-hexylaluminum; alkylolithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium and 1,4-dilithiobutane; and dialkylzinc compounds such as diethylzinc and dibutylzinc.

Examples of suitable cobalt catalysts include the following composed of cobalt or cobalt compounds: Raney cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyldithiocarbamate, cobalt anilinium nitrite and cobalt dinitrosyl chloride. It is particularly advantageous to use the above in combination with a dialkylaluminum monochloride such as diethylaluminum monochloride or diisobutylaluminum monochloride; a trialkylaluminum such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum or tri-n-hexylaluminum; an alkyl aluminum sesquichloride such as ethylaluminum sesquichloride; or aluminum chloride.

Polymerization using the Group VIII catalysts described above, and especially a nickel or cobalt catalyst, can generally be carried out by a process in which the catalyst is continuously charged into the reactor together with the solvent and butadiene monomer, and the reaction conditions are suitably selected from a temperature range of 5 to 60° C. and a pressure range of atmospheric pressure to 70 plus atmospheres, so as to yield a product having the above-indicated Mooney viscosity.

It is also desirable for the second polybutadiene in component (b) to satisfy the relationship:

$$20A-750 \leq \eta \leq 20A-550$$

wherein  $\eta$  is the viscosity of the second polybutadiene at 25° C. as a 5 wt % solution in toluene and A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene.



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The viscosity  $\eta$  is preferably at least 20A–700, more preferably at least 20A–680, and most preferably at least 20A–650, but preferably not more than 20A–560, more preferably not more than 20A–580, and most preferably not more than 20A–590. The use of a polybutadiene having such an optimized relationship of  $\eta$  and A, that suggests the high linearity of polybutadiene molecules, is effective for conferring better resilience and workability.

The second polybutadiene generally accounts for at least 30 wt %, preferably at least 50 wt %, and most preferably at least 70 wt %, and up to 100 wt %, preferably up to 90 wt %, and most preferably up to 80 wt %, of the diene rubber (b). By including the second polybutadiene within component (b) in the foregoing range, even better extrudability and hence, workability during manufacture can be conferred.

The solid core in the golf balls of the invention is molded from a rubber composition containing as essential components specific amounts of (c) an unsaturated carboxylic acid and/or metal salt thereof, (d) an organosulfur compound, (e) an inorganic filler and (f) an organic peroxide per 100 parts by weight of the base rubber.

Specific examples of unsaturated carboxylic acids that may be used as component (c) include acrylic acid, methacrylic acid, maleic acid and fumaric acid. Acrylic acid and methacrylic acid are especially preferred.

Specific examples of unsaturated carboxylic acid metal salts that may be used as component (c) include the zinc and magnesium salts of unsaturated fatty acids such as zinc methacrylate and zinc acrylate. Zinc acrylate is especially preferred.

The unsaturated carboxylic acid and/or metal salt thereof used as component (c) is included in an amount, per 100 parts by weight of the base rubber, of at least 10 parts by weight, preferably at least 15 parts by weight, and most preferably at least 20 parts by weight, but not more than 60 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much component (c) results in excessive hardness, giving the golf ball a feel upon impact that is difficult for the player to endure. On the other hand, too little component (c) undesirably lowers the resilience.

The organosulfur compound (d) of the rubber composition is essential for imparting good resilience. Exemplary organosulfur compounds include thiophenol, thionaphthol, halogenated thiophenols, and metal salts thereof. Specific examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, and zinc salts thereof, such as the zinc salt of pentachlorothiophenol; and organosulfur compounds having 2 to 4 sulfurs, such as diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides. Diphenyldisulfide and the zinc salt of pentachlorothiophenol are especially preferred.

The organosulfur compound (d) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.2 part by weight, and most preferably at least 0.5 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much organosulfur compound results in an excessively low hardness, whereas too little makes it impossible to enhance the resilience.

Examples of inorganic fillers that may be used as component (e) include zinc oxide, barium sulfate and calcium

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carbonate. The inorganic filler (e) is included in an amount, per 100 parts by weight of the base rubber, of at least 5 parts by weight, preferably at least 7 parts by weight, more preferably at least 10 parts by weight, and most preferably at least 13 parts by weight, but not more than 80 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much or too little inorganic filler makes it impossible to achieve a golf ball core having an appropriate weight and good rebound characteristics.

The organic peroxide (f) may be a commercial product, suitable examples of which include Percumil D (manufactured by NOF Corporation), Perhexa 3M (manufactured by NOF Corporation) and Lupercos 231XL (manufactured by Atochem Co.). If necessary, two or more different organic peroxides may be mixed and used together.

The organic peroxide (f) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.3 part by weight, more preferably at least 0.5 part by weight, and most preferably at least 0.7 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much or too little organic peroxide makes it impossible to achieve a ball having a good feel upon impact and good durability and rebound characteristics.

If necessary, the rubber composition may also include an antioxidant, suitable examples of which include such commercial products as Nocrac NS-6, Nocrac NS-30 (both made by Ouchi Shinko Chemical Industry Co., Ltd.), and Yoshinox 425 (made by Yoshitomi Pharmaceutical Industries, Ltd.). The use of such an antioxidant in an amount, per 100 parts by weight of the base rubber, of at least 0 part by weight, preferably at least 0.05 part by weight, more preferably at least 0.1 part by weight, and most preferably at least 0.2 part by weight, but not more than 3 parts by weight, preferably not more than 2 parts by weight, more preferably not more than 1 part by weight, and most preferably not more than 0.5 part by weight, is desirable for achieving good rebound characteristics and durability.

The solid core of the invention can be produced by vulcanizing and curing the above-described rubber composition using a method like that employed with known rubber compositions for golf balls. For example, vulcanization may be carried out at a temperature of 100 to 200° C. for a period of 10 to 40 minutes.

In the practice of the invention, the solid core has a hardness which is suitably adjusted according to its manner of use in the various golf ball constructions that may be employed and is not subject to any particular limitation. The core may have a cross-sectional hardness profile which is flat from the center to the surface thereof, or which varies from the center to the surface.

It is recommended that the solid core have a deflection, when subjected to a load of 980 N (100 kg), of at least 2.0 mm, preferably at least 2.5 mm, more preferably at least 2.8 mm, and most preferably at least 3.2 mm, but not more than 6.0 mm, preferably not more than 5.5 mm, more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. Too small a deformation may worsen the feel of the ball upon impact and, particularly on long shots such as with a driver in which the ball incurs a large deformation, may subject the ball to an excessive rise in spin, reducing the carry. On the other hand, if the solid core is too soft, the golf ball tends to have a dead feel when hit, an inadequate

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rebound that results in a poor carry, and a poor durability to cracking with repeated impact.

It is recommended that the solid core in the inventive golf ball have a diameter of at least 30.0 mm, preferably at least 32.0 mm, more preferably at least 34.0 mm, and most preferably at least 35.0 mm, but not more than 40.0 mm, preferably not more than 39.5 mm, and most preferably not more than 39.0 mm.

It is also recommended that the solid core have a specific gravity of at least 0.9, preferably at least 1.0, and most preferably at least 1.1, but not more than 1.4, preferably not more than 1.3, and most preferably not more than 1.2.

The golf ball of the invention is a multi-piece solid golf ball having a cover composed of at least two layers which are referred to herein as the "inner cover layer" and the "outer cover layer." Such cover layers can be produced from known cover stock. The cover stocks used to make both cover layers in the inventive golf ball may be composed primarily of a thermoplastic or thermoset polyurethane elastomer, polyester elastomer, ionomer resin, ionomer resin having a relatively high degree of neutralization, polyolefin elastomer or mixture thereof. Any one or mixture of two or more thereof may be used, although the use of a thermoplastic polyurethane elastomer, ionomer resin or ionomer resin having a relatively high degree of neutralization is especially preferred.

Illustrative examples of thermoplastic polyurethane elastomers that may be used for the above purpose include commercial products in which the diisocyanate is an aliphatic or aromatic compound, such as Pandex T7298, Pandex T7295, Pandex T7890, Pandex TR3080, Pandex T8290, Pandex T8295 and Pandex T1188 (all manufactured by DIC Bayer Polymer, Ltd.). Illustrative examples of suitable commercial ionomer resins include Surlyn 6320, Surlyn 8945, Surlyn 9945 and Surlyn 8120 (both products of E. I. du Pont de Nemours and Co., Inc.), and Himilan 1706, Himilan 1605, Himilan 1855, Himilan 1557, Himilan 1601 and Himilan AM7316 (all products of DuPont-Mitsui Polychemicals Co., Ltd.).

Together with the primary material described above, the cover stock may include also, as an optional material, polymers (e.g., thermoplastic elastomers) other than the foregoing. Specific examples of polymers that may be included as optional constituents include polyamide elastomers, styrene block elastomers, hydrogenated polybutadienes and ethylene-vinyl acetate (EVA) copolymers.

The multi-piece solid golf ball of the invention can be manufactured by any suitable known method without particular limitation. In one preferred method, the solid core is placed within a given injection mold, following which a predetermined method is used to successively inject over the core the above-described inner and outer cover layer materials. In another preferred method, each of the cover stocks is formed into a pair of half cups, and the resulting pairs are successively placed over the solid core and compression molded.

In the golf balls of the invention, it is critical that the outer cover layer have a lower Shore D hardness than the inner cover layer.

It is recommended that the inner cover layer have a Shore D hardness of at least 50, preferably at least 51, more preferably at least 52, and most preferably at least 53, but not more than 80, preferably not more than 75, more preferably not more than 70, and most preferably not more than 65.

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It is recommended that the outer cover layer have a Shore D hardness of at least 35, preferably at least 40, more preferably at least 45, and most preferably at least 48, but not more than 60, preferably not more than 58, more preferably not more than 56, and most preferably not more than 54.

As noted above, in the practice of the invention the outer cover layer must have a lower Shore D hardness than the inner cover layer. It is advantageous for the inner and outer cover layers to have a difference in Shore D hardness of at least 2, preferably at least 5, more preferably at least 7, and most preferably at least 9 Shore D hardness units, but not more than 30, preferably not more than 25, and most preferably not more than 20 Shore D hardness units.

It is recommended that the inner and outer cover layers have a respective thickness of at least 0.7 mm, and preferably at least 1.0 mm, but not more than 3.0 mm, preferably not more than 2.5 mm, even more preferably not more than 2.0 mm, and most preferably not more than 1.6 mm.

The multi-piece solid golf ball of the invention can be manufactured for competitive use by imparting the ball with a diameter and weight which conform with the Rules of Golf; that is, a diameter of at least 42.67 mm and a weight of not more than 45.93 g. It is recommended that the diameter be no more than 44.0 mm, preferably no more than 43.5 mm, and most preferably no more than 43.0 mm; and that the weight be at least 44.5 g, preferably at least 45.0 g, more preferably at least 45.1 g, and most preferably at least 45.2 g.

Multi-piece solid golf balls according to the present invention have a good, soft feel upon impact and an excellent spin performance that enable the ball to travel a greater distance when played.

## EXAMPLES

The following examples and comparative examples are provided to illustrate the invention, and are not intended to limit the scope thereof.

### Examples 1-5 & Comparative Examples 1-4

The core materials shown in Table 2 were formulated in the indicated amounts per 100 parts by weight of polybutadiene material composed of polybutadiene types (1) to (7) below in the proportions shown in Table 1. The resulting core formulations were blended in a kneader or on a roll mill, then molded under applied pressure at 150° C. for 20 minutes to form solid cores having a diameter of about 36.4 mm.

#### Types of Polybutadiene

- (1) BR01, made by JSR Corporation
- (2) BR11, made by JSR Corporation
- (3) UBE101, made by Ube Industries, Ltd.
- (4) HCBN-4, an experimental grade of polybutadiene made by JSR Corporation
- (5) HCBN-2, an experimental grade of polybutadiene made by JSR Corporation
- (6) Experimental grade #9100081 made by Firestone
- (7) Experimental grade #9100069 made by Firestone

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TABLE 1

Type	Catalyst	cis-1,4 content, %	1,2 vinyl content, %	Mooney viscosity (A)	Mw/Mn (B)	η	10B + 5	10B + 60	20A - 550
Polybutadiene									
(1)	Ni	96	2.5	44	4.2	150	47	102	330
(2)	Ni	96	2	44	4.4	270	49	104	330
(3)	Co	95	3	38	4.2	130	47	102	210
(4)	Nd	96	1.1	44	3.5	390	40	95	330
(5)	Nd	96	0.9	40	3.3	280	38	93	250
(6)	Nd	95	1.5	56	2.6	370	31	86	570
(7)	Nd	96	1.3	48	2.5	280	30	85	410

TABLE 2

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
Rubber formulation (pbw)									
(1)						50			
(2)	70	30	50		50	50		50	
(3)				50			50		50
(4)	30								
(5)				50	50		50	50	50
(6)		70							
(7)			50						
Core formulation (pbw)									
Polybutadiene	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.4	1.4	1.4	0.7	0.7	1.4	1.4	1.4	1.4
1,1-Bis(t-butylperoxy)-3,3,5-trimethylcyclohexane				0.3	0.3				
Zinc oxide	18	18	15.5	27	26	26	28.5	27	26
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc acrylate	27	27	31	30	32	32	28	30	32
Zinc salt of pentachlorothiophenol	1	1	2	1	1	1	0	1	1

The resulting solid cores were tested as described below to determine their deformation under 980 N (100 kg) loading and their rebound. The results are shown in Table 4.

Deformation Under 980 N Loading

Measured as the deflection (mm) of the solid core when subjected to a load of 980 N (100 kg).

Rebound

The initial velocity of the solid cores was measured with the same type of initial velocity instrument as used by the official regulating body—the United States Golf Association (USGA). Each rebound value shown in Table 4 is the difference between the initial velocity of the solid core obtained in that particular example and the initial velocity of the solid core obtained in Comparative Example 2.

In each example, the resulting solid core was placed in a given mold and the appropriate resin shown in Table 3 was injection-molded over the core, thereby producing an inner layer-covered core having a diameter of about 39.7 mm. The covered core was then transferred to a given mold, and the appropriate resin shown in Table 3 was injection molded over the covered core, yielding a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g. Trade names appearing in Table 3 are described below.

Himilan: An ionomer resin produced by DuPont-Mitsui Polychemicals Co., Ltd.

Surlyn: An ionomer resin produced by E. I. du Pont de Nemours and Co.

Dynaron: An E-EB-E block copolymer produced by JSR Corporation

Pandex: A polyurethane elastomer produced by Bayer-DIC Polymer, Ltd.

The properties of the resulting golf balls were determined as described below. The results are shown in Table 4.

Material Properties

The Shore D hardnesses of the inner cover layer and the outer cover layer were measured with a durometer by the test method described in ASTM D2240.

Golf Ball Properties

The carry and total distance were measured when the ball was hit at a head speed (HS) of 50 m/s with a driver (No. 1 Wood) mounted on a swing machine.

Feel

The feel of the ball when actually shot with a driver (No. 1 Wood) and putter was rated by five professional and five top-caliber amateur golfers as “Too hard,” “Good” or “Too soft.” The rating assigned most often to a particular ball was used as that ball’s overall rating.

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TABLE 3

	A	B	C	D	E	F	G	
Formulation (pbw)								5
Himilan 1706	50	70						
Himilan 1605	50							
Himilan 1557							20	
Himilan 1855							30	10
Himilan AM7316		12						
Surlyn 8945			35					
Surlyn 9945			35					
Surlyn 8120				100			50	
Dynaron 6100P			30					15
Pandex T8290					50			
Pandex T8295					50	100		
Behenic acid		16						
Magnesium oxide		2						
Titanium dioxide	4	2	4	4	2.7	2.7	4	20

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Japanese patent application Ser. No. 2001-163238 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising

100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, being synthesized using a rare-earth catalyst and satisfying the relationship:  $10B + 5 \leq A \leq 10B + 60$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a),

TABLE 4

[illegible]

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(c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both,

(d) 0.1 to 5 parts by weight of an organosulfur compound,

(e) 5 to 80 parts by weight of an inorganic filler,

(f) 0.1 to 5 parts by weight of an organic peroxide;

the inner cover layer has a Shore D hardness of 50 to 80;

the outer cover layer has a Shore D hardness of 35 to 60; and

the outer cover layer has a lower Shore D hardness than the inner cover layer.

2. The golf ball of claim 1, wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of not more than 55, and satisfies the relationship:

$$\eta \leq 20A - 550,$$

wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene and  $\eta$  is the viscosity of the second polybutadiene, in mPa·s, at 25° C. as a 5 wt % solution in toluene.

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3. The golf ball of claim 1 wherein said polybutadiene (a) is synthesized by using neodymium catalyst.

4. The golf ball of claim 1 wherein said polybutadiene (a) has a Mooney viscosity ( $ML_{1+4}$ , 100° C.) of 40 to 60.

5. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 5 units.

6. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 7 units.

7. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 9 units.

8. The golf ball of claim 1, wherein said ball is three-piece construction consisting of a solid core, an inner cover layer and an outer cover layer.

9. The golf ball of claim 2, wherein the second polybutadiene in component (b) is synthesized using a Group VIII catalyst.

\* \* \* \* \*